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A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

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AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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SEPTEMBER, 1909

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THE

PHYSICAL REVIEW.

ON THE SECONDARY RADIATION PRODUCED FROM SOLIDS, SOLUTIONS, AND PURE LIQUIDS, BY THE β RAYS OF RADIUM.

By S. J. Allen.

THE secondary radiation, however produced, is of the greatest interest and importance, since it affords a possible means of deciding whether or no the atom can be disintegrated by an external agency. The aim of experimenters has been to accumulate facts which would tend to prove or disprove this important point. In order to account for the production of secondary radiation by γ and Roentgen rays, two theories at the present time are in prominence.

J. J. Thomson considers the wave front of a beam of X-rays to consist of an amount of energy concentrated in bundles, the space in between containing no energy. As these bundles of concentrated energy pass over the atoms of a substance enough of the energy is absorbed to destroy in some of the atoms the equilibrium, and an expulsion of corpuscles results. On this theory the secondary radiation is derived from the bombarded atoms and at the expense of the energy of the primary beam.

I have great difficulty myself in getting a conception of what concentrated bundles of energy mean, and of the mechanism whereby such a system could be propagated; consequently the above theory of secondary radiation does not appear to me very explanatory of the known facts. It certainly does not lead to an explanation in terms of more simple ideas.

On the other hand, Bragg has advanced a totally different theory[1] of γ and X-rays to account for his own experimental results on the secondary radiation, and criticizes quite strongly J. J. Thomson's theory. On his view the secondary rays are derived from the primary beam and not from the bombarded atoms. He assumes the beam of γ or X-rays to be made up of a number of electric doublets travelling at high speed, and each doublet as composed of a negative and positive election of the same charge and mass, and held together by a bond which under ordinary circumstances is strong enough to prevent rupture. When this doublet penetrates among the atoms of a substance they may in some cases be broken up, the positive parts remaining at rest in the substance, while the negative parts are scattered in all directions and form the secondary radiation.

In the first place, in order to make this theory workable, Bragg has to assume the existence of a positive electron of the same mass as the negative, which is a conception that is not at the present time borne out by any experimental evidence. Next, he assumes in the case of γ rays that the doublet is expelled entire from a radioactive atom, whereas in ordinary matter it can be ruptured quite readily. If there is a positive electron of the same mass as the negative, then it must obey, according to all our present views on electrical charged bodies, the same laws that the negative does, the only difference being one of direction. In the determination of the velocity, and ratio e/m, for the positive particle by the electric and magnetic deviations the same formulas are used as in the case of the negative electron, no distinction being made except that the direction of deviation is opposite. It is then very difficult to see how the positive part of such a doublet could behave in any way different from the negative. The positive electron would not be brought to rest after rupture, but would on the average have the same velocity as the negative.

A metal plate struck by a beam of doublets ought therefore to show both on the incident and emergent sides the presence of secondary or scattered positive corpuscles as well as negative. This we know is contrary to the known experimental facts.

[1] Phil. Mag., December, 1908.

The doublet theory of Bragg, while it may agree closely with his experimental facts, does not seem therefore justifiable on our present views of positive electricity.

The secondary β radiation from solids has been studied by a number of experimenters and a great deal of valuable information has been obtained, but as far as I can learn no work has been done on salt solutions, and pure liquids, a field which ought to be productive of important results.

The present work of the author on solutions and liquids was undertaken to see if the results obtained would agree in any way with those already obtained for the pure elements, and especially to test whether the atomic weight law would hold for such complex systems of atoms as we there have to deal with.

A number of experiments were also made on the radiation from pure metals and powdered metallic salts in order to compare their results with those from solutions and liquids. The experiments on the metals and salts to a great extent parallel those of other investigators, and wherever possible due credit will be given.

Before describing the experiments it may be well to discuss the principal facts in regard to the secondary β radiation.

It was early shown that by far the greater proportion of secondary β rays consisted of electrons traveling with speeds only little inferior to those of the primary. The author[1] showed that the velocities of the secondary rays varied with different materials being greatest for lead. The velocity in the case of lead was measured, and found to be of the order 2×10^{10} cm. per second for the highest speed rays, which is only slightly less than that of the primary electrons. It is also well known that the secondary rays in turn produce tertiary rays of the same nature but a little less velocity.

It has recently been shown by McClelland[2] that the amount of secondary radiation from a given material can be considered as made up of two parts, the first representing what he calls the reflected radiation and the second the true secondary radiation. The reflected part does not vary much with the atomic weight of the bombarded and is considered by McClelland to be some of the pri-

[1] Phys. Ser., August, 1906.
[2] Phil. Proc., July, 1908.

mary rays which have bent backward without entering or causing any disintegration of the atom. The true secondary radiation is a function of the atomic weight of the material struck rapidly decreasing with decreasing atomic weights. The amount of secondary rays also varies with the angle of incidence of the primary beam, being least for normal incidence. The true secondary rays are thought by McClelland to be due to a disintegration of the bombarded atoms.

Crowther[3] has shown that the primary β rays undergo a scattering when they penetrate into a material but that this scattering is complete after a certain distance has been traversed.

There seems to be a great deal of evidence therefore that a portion at least of the secondary rays from solid substances is due to scattering of the primary. Whether the remainder is derived from the atoms of the substance, or from the primary beam, does not appear so conclusive.

We are certain, however, that almost, if not quite all, the total secondary radiation from a solid is of the same nature as the primary. Part at least of the amount from any given pure element seems to be a function of its atomic weight.

EXPERIMENTAL ARRANGEMENT.

It has been pointed out by several investigators that the method of measuring the secondary radiation used by the early experimenters was not suitable for obtaining the true relative values of the radiation from different materials, on account of the variation in the velocities of the rays. The lower the velocity the greater the ionizing power of the rays, and consequently the radiation from the atoms of low atomic weight would be exaggerated over that for the high atomic weight ones.

The ionization chamber ought therefore to be such a size that the rays could be completely absorbed before striking the walls. Now such an arrangement would be very difficult to obtain, since it would necessitate a very large ionization chamber, a very high potential to saturate the enclosed air, and a narrow beam of the secondary rays so that they could not strike the side walls of the chamber in their flight.

[1] Phil. Mag., October, 1906.

The best that can be done is to approximate to the ideal arrangement by making the chamber as large as possible consistent with the available conditions of the experiment.

Bragg[1] has sought to overcome this difficulty in the following manner: Two concentric hemispherical shells were used to form the ionization chamber instead of the customary rectangular or cylindrical chambers with a central electrode. The outer hemisphere was connected to an electrometer, while the inner one constructed of very thin aluminum foil was joined to a battery. The radium was placed in a block of lead fastened to the inner side of the lower electrode at the top. The metal plate to be examined for the secondary rays was placed in a horizontal plane at the diameter of the two hemispheres. The beam of β rays fell at nearly normal incidence upon the metal plate, and the secondary rays there produced passed in all directions through the thin aluminum shell into the space between the two hemispheres.

By this arrangement practically all the secondary rays produced get into the ionization chamber, and therefore a much larger amount can be measured than by any other method. Sheets of tinfoil are then placed over the thin aluminum foil and the ionization measured with the increasing thickness until the secondary rays are practically all absorbed. If we assume that the absorption in air follows the same general law as it does in tinfoil the above experimental process would be practically the same as removing the outer hemisphere to greater and greater distances from the inner, since the solid angle would be the same in all cases.

If the readings are therefore plotted in the form of curves, in which the ordinates represent ionization, and the abscissæ thickness of absorbing layer, the area of such curves will represent numbers proportional to the total secondary radiation. The ratios of these areas for various radiating substances will then represent more correctly the relative radiating powers than the old method.

In the present investigations the author has made use of two methods, which will be referred to as method *A* and method *B*.

Method A. — The arrangement of this method is shown in Fig 1, and is almost the same as that used by Bragg, differing only in the

[1] Phil. Mag., October, 1908.

position of the radium, and consequently in the angle of incidence of the primary beam.

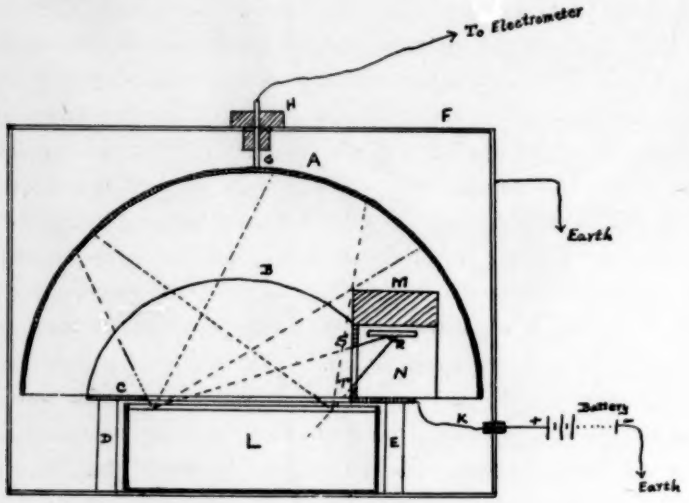


Fig. 1.

It may be briefly described as follows :

A is a hemispherical shell fastened to a metal rod G which passes through and is insulated from the metal case F by means of the ebonite block H. A wire from this hemisphere is joined to the electrometer. Supported on the insulating ebonite pillars D and E is the circular brass plate C which is joined to the battery by means of the wire K. Fastened to this plate is a black of wood N, which supports the small glass tube R containing 5 milligrams of radium bromide. The front of this wooden block is covered with a lead plate in which an opening is cut to allow a well-defined pencil of β rays to emerge. B is the inner shell made of thin aluminum foil stretched on a number of fine wires joined to the plate C. In the plate C is cut an opening which is considerably larger than the area of the beam of β rays at that point, thus insuring that none of the β rays shall strike the sides of this opening. A block of lead M is placed over the radium so as to cut down the γ radiation as much as possible.

L represents a cylindrical glass vessel in which is placed the substance to be tested for secondary rays.

The upper surface of the substance, whether solid or liquid, was always placed at the same height, and level, so that all readings would be comparable with each other.

The secondary rays emerge from the substance bombarded in all directions and passing upward through the thin aluminum ionize the air between the hemispheres.

The electrometer used in these experiments was the null reading instrument devised by the author and already described in several papers. The charge of electricity communicated to the quadrants from the shell A is balanced by an equal amount of opposite sign furnished by the standard. In the present case the quantity of charge was too great to be balanced by a layer of uranium oxide and so a uniform layer of rather weak radium bromide was used.

A small amount of radium was dissolved in water and a few drops spread on a metal plate, and rubbed over the surface uniformly. After drying the surface of the plate was rubbed over with a fine emery cloth until the amount of radium left was just sufficient for the experiment in hand.

This standard was found to act excellently, and no appreciable variation in its activity was observed, and no trouble was experienced from the very small amount of emanation which may have been liberated.

The balance part of such an instrument is independent of changes in the potential of the electrometer needle, which was a very advantageous feature in the present experiments, since the γ rays of the radium passing through the walls of the testing vessel and through the case of the electrometer discharged the needle quite rapidly. In fact the needle had to be recharged about every 20 minutes.

With a electrometer using the "rate of leak" method great difficulty would have been experienced from this cause.

Method B. — The arrangement of this method is shown in Fig. 2. A is a cylinder of zinc 60 cm. long by 15 cm. in diameter. This formed the outer electrode and was joined to one pole of the battery. The central electrode consisted of a brass rod B passing through the ebonite insulating block D, and joined to the electrometer by a wire as indicated. A guard ring E connected to earth was fastened between A and B.

The bottom of the cylinder was closed with a thin sheet of aluminum. The cylinder was supported on two insulating blocks H and F, and had its axis inclined at a considerable angle to the vertical.

The tube containing the radium was fastened inside F and the rays allowed to emerge in the same manner as already described in method A. The size of the beam and the angle of incidence was the same as in method A.

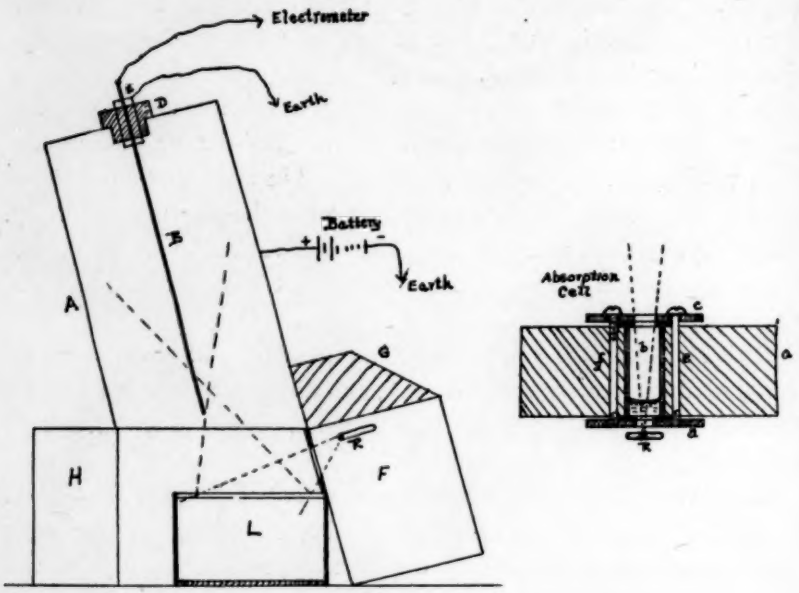


Fig. 2.

A block of lead G was placed over the radium so as to cut down the γ rays as much as possible.

The method of operation was precisely the same as in method A.

RADIATION FROM PURE METALS.

These experiments to a certain extent parallel those of McClelland and Bragg, but it was thought advisable to perform them in order to be able to compare their results with those of the author, and so obtain a check on the accuracy of the various results. The department was in the fortunate possession of a number of thick plates of pure metals which were at my disposal.

The plates were placed directly under the opening in the brass plate C (Fig. 1) and always at a fixed distance away from it. The area of the plates with the exception of the gold, platinum and palladium, was greater than the area of the incident beam of β rays. In all cases the thickness of the plates was more than sufficient to absorb all the incident rays.

In order to make the readings for the gold, platinum and palladium plates comparable with those for the other metals, a plate of lead of the same area was tested; and by means of this reading and that of the large lead plate, the readings for the gold, platinum and palladium could be corrected for their smaller area. On this account the results for these metals are perhaps not quite so accurate as the others.

The ionization between the two hemispherical shells is due to γ radiation, secondary rays caused by the γ rays, secondary β rays from the metal plates, and possibly a small amount of secondary β rays produced where the β rays strike the edges of the opening in the lead plate. In fact it is impossible to narrow down a beam of β rays without introducing at the same time a small amount of secondary rays.

Two readings were taken: (a) with a sheet of lead placed over the opening ST of sufficient thickness to cut off the β radiation, (b) without this sheet of lead.

The difference ($b - a$) between these two readings was taken as a measure of the secondary rays from the plate under test.

A sheet of tinfoil was then placed over the aluminum foil hemisphere and the readings (a and b) again taken.

This operation was repeated until the secondary rays were practically all absorbed by the tinfoil. The reading (a) decreased only a very little as successive layers of tinfoil were added.

The results of these experiments are shown in Table I. The reading for lead is taken arbitrarily as 1,000 and the others calculated in terms of it.

The third column represents the radiation through the thin aluminum foil which absorbed extremely little of the radiation. The next six columns represent the radiation through the various thicknesses of tinfoil.

If we examine the second and third columns we see that, with the exception of palladium, the radiation follows the order of the atomic weight of the struck substance. The values for palladium and silver are very close to one another, and the difference is probably due to experimental errors, since as already stated the area of the palladium plate was less than that of the silver.

If the results are plotted, having as ordinates the radiations and as abscissæ the atomic weights, the resulting curve is fairly regular but it is far from being a straight line, the radiations for the low atomic weight atoms being much greater in proportion than those from the high atomic weight atoms.

When compared with the results of Bragg, it is seen that his results for the light atoms are much less relatively to the high ones than are those of the author. In Bragg's experiments the primary rays fell upon the plate at nearly normal incidence, whereas in the author's arrangement the angle of incidence was between 70° and 80°.

TABLE I.

Substance.	Atomic Weight.	Radiation Uncovered.	Radiation .00105 cm.	Radiation .00210 cm.	Radiation .00315 cm.	Radiation .00725 cm.	Radiation .0155 cm.	Radiation .0237 cm.	Area of Curve.
Lead	207	1,000	760	570	460	191	57	27	1,000
Bismuth	209	1,005							
Gold	197	970	733	557	451	189	56	27	954
Mercury	200	990	755	570	460	191	57	27	985
Platinum	195	966							
Antimony	120	895							
Cadmium	112	870							
Silver	108	835	600	435	347	143	37	18	725
Palladium	107	839	620	446	363	160	37	18	740
Zinc	65	742	500	373	310	114	30	14	600
Copper	63	732	484	361	298	110	29	14	593
Iron	56	660	440	335	260	93	24	12	464
Sulphur	32	578							
Aluminum	27	500	343	245	190	64	13	6	353
Carbon	12	347	220	156	110	43	8		220

Now the work of McClelland has shown that when the angle of incidence was increased the ratio between the radiation for a light atom and a heavy one was much reduced. For example, at 75°

incidence the radiation given by him for lead was 58, while that for aluminum was 27, a ratio of $\frac{27}{58} = .466$. The ratio in the case of the author's results is .500.

It thus seems very probable that the total secondary radiation from a plate struck by β rays depends to a great extent upon the angle of incidence of the β rays, as stated by McClelland.

It is also clear from the author's results that the secondary radiation increases with the atomic weight.

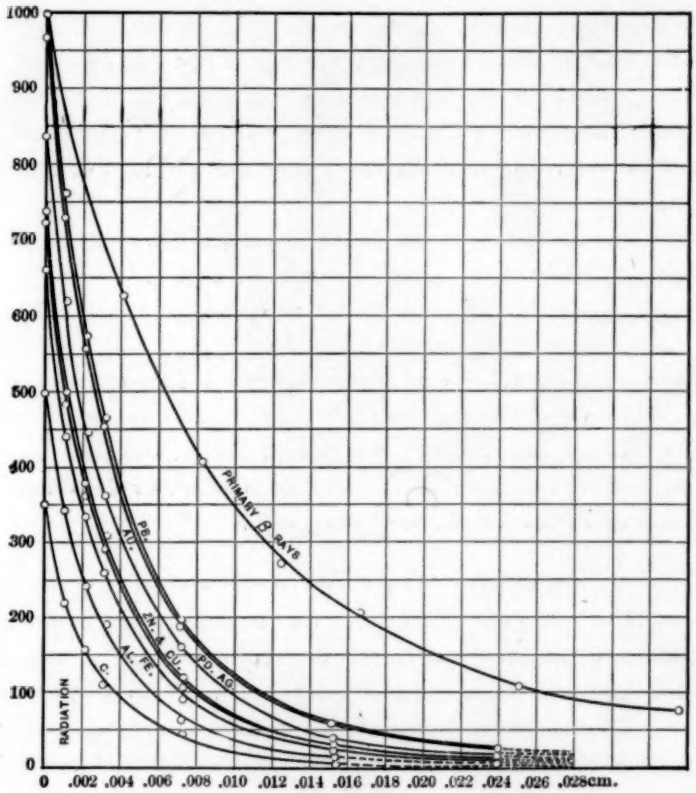


Fig. 3.

In Fig. 3 the results from the above table are plotted in the form of curves, the ordinates representing the radiation and the abscissæ the thickness of the tinfoil. The absorption curve for the lead is not very far different from the values given by Bragg for the same

metal, but when we come to examine those for the lighter atoms we find a great difference.

In Bragg's results the radiation from aluminum, for example, decreases very much more rapidly than it does in the results of the author.

It is thus evident that when a large angle of incidence is used the average penetrating power of the rays from substances of low atomic weight is much greater than when the angle of incidence is normal.

If we we examine the figures in columns 8 and 9 of Table I. it is seen that after the rays have gone through .0155 cm. of tinfoil the remaining portion is of about the same penetrating power for all the substances, being cut to half value in .008 cm. of tinfoil. All the substances observed give off a small proportion of rays of the same penetrating power.

In the last column of Table I. are expressed the relative areas of the surfaces below the absorption curves of Fig. 3.

These areas were obtained by means of a planimeter. The figures thus obtained represent the total secondary radiation of the various substances relative to that of lead, and they decrease much more rapidly with decrease of atomic weight than those in column 3.

This is in agreement with the results of Bragg, and show that the old method of using a shallow ionization chamber does not give true relative values for the secondary rays.

RADIATION FROM POWDERED SALTS.

A short series of tests were made on powdered salts, to see if the radiation bore any relation to the molecular weights of the salts. If the radiation from a pure element is a function of the atomic weight, we should expect as a first approximation the radiation of a salt to be a function of the sum of the atomic weights of its chemical constituents, that is, of its molecular weight.

The salts were powdered very fine in a mortar, and then placed in a shallow cardboard box, the surface of the salt being pressed down as smooth as possible by a brass weight. The area of the salt was the same as the metal plates in the previous experiments and the method of testing the same.

The results are represented in Table II., the readings being expressed in terms of lead equal to 1,000.

An examination of this table shows that the radiation from powdered salts does not follow in general the order of the molecular weights. Lead carbonate has a greater radiation than lead nitrate although the molecular weight is less. Potassium chloride also has a greater radiation than its molecular weight would warrant. The same is true of lithium and sodium chlorides. The effect of an atom of high atomic weight can, however, be readily seen by an increase in the radiation. Lithium chloride has a greater radiation than lithium carbonate though of much less molecular weight.

This is perhaps due to the presence of the chlorine atoms giving more radiation than the carbonate.

TABLE II.

Substance.	Chemical Formula.	Molecular Weight.	Intensity of Radiation. Pb = 1,000.
Lead carbonate	$PbCO_3$	327	954
Lead nitrate	$Pb(NO_3)_2$	331	892
Lead acetate	$Pb(C_2H_3O_2)_2$	325	885
Mercuric chloride	$HgCl_2$	271	878
Barium chloride	$BaCl_2$	208	754
Strontium chloride	$SrCl_2$	159	606
Copper chloride	$CuCl_2$	134	576
Manganese chloride	$MnCl_2$	126	500
Potassium chloride	KCl	75	555
Calcium chloride	$CaCl_2$	111	480
Sodium chloride	NaCl	59	500
Lithium chloride	LiCl	43	490
Lithium carbonate	Li_2CO_3	74	362
Sugar (cane)	$C_{12}H_{22}O_{11}$	342	330

Let us examine the bichlorides more in detail, arranging them in the following table.

Substance.	Molecular Wt.	Radiation.	
		Total.	Total—Cl_2.
$Hg+Cl_2$	200+71	878	638
Ba + "	137+ "	754	514
Sr + "	88+ "	606	366
Cu + "	63+ "	576	336
Mn+ "	55+ "	500	260
Ca + "	40+ "	480	240

All these salts have the same amount of chloride which we will assume to give a constant radiation. The difference between this constant radiation and the total radiation for any salt ought to be due to the presence of metal. We have no means of knowing just what this constant amount would be, but in the case of calcium chloride I have assumed it to be half the total, which is probably somewhere near the truth, since the atomic weights of calcium and chloride are nearly equal. In the last column are represented these differences and they show, if the above reasoning is true, that the radiation due to the presence of a metal in a bichloride salt is a function of the atomic weight of the metal. The same conclusion may possibly hold for other groups of metallic salts, such as the carbonates, nitrates, sulphates, etc.

When we compare, however, the salts regardless of their chemical grouping and consider only the molecular weights we do not get results which are very consistent. Cane sugar although having a high molecular weight has only a low radiation.

RADIATION FROM AQUEOUS SOLUTION OF SALTS.

In these experiments the salts were dissolved in distilled water, the solutions being made up to so many grams of salt per 1,000 grams of water. The number of salts which are readily soluble in water is not great, and the number of tests made were therefore somewhat limited, since for many of the salts in order to get a fairly large radiation the concentration had to be great.

The solution to be tested was poured into the glass cylindrical cell described above, the surface of the liquid always being at the same level and depth.

The reading for the pure water was taken frequently during a series of tests on the solutions, so as to make correction in case of any changes. The solutions were carried in all cases to saturation.

The results are shown in Table III. Under concentration we have three columns, *a*, *b*, *c*. In column *a* the concentration is expressed in grams of dissolved salt per 1,000 grams of water, in column *b* the same divided by the molecular weight of the salt, in column *c* the values of column *b* corrected for the valency of the metal part of the salt. The radiations are expressed both in terms

of lead as 1,000 and in term of water as 100. When a salt is dissolved in water there is an increase of volume of the solution, and therefore the amount of water in the fixed volume of the glass testing cell will get less and less as the concentration is increased. The increase of radiation due to a solid substance dissolved in water will consequently always be a differential effect of the increase caused by the salt and the decrease caused by the water displaced. If by chance the molecules of a liquid dissolved in water should have the same specific radiation as the molecules of the water, then we would expect the total radiation from the solution to remain constant, since the increase due to the dissolved liquid would be just balanced by

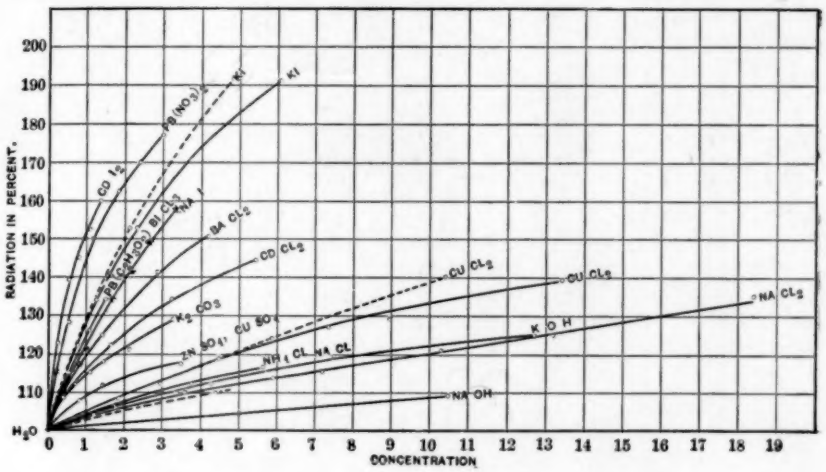


Fig. 4.

the decrease due to the water displaced. That is, a cubic centimeter of the solution would always contain the same number of molecules of both kinds.

The results given in Table III. are plotted in the form of curves in Fig. 4, the ordinates representing the total radiation of the solutions, with water alone taken as 100 per cent., and the abscissæ the concentration in gram molecular weights per 1,000 grams of water. In the figures here given pure water has a radiation of 320 in terms of lead taken as 1,000.

If now we examine these curves in detail we can I think bring out the following facts:

TABLE III.

Substance.	Chemical Formula.	Concentration.			Radiation Pb=1,000.		Radiation Water=100.	
		a	*b*	*c*	Salt Alone.	Total.	Salt Alone.	Total.
Lead nitrate	$Pb(NO_3)_2$	100	.30	.60	88	408	28	128
" "	(331)	200	.60	1.20	156	476	50	150
" "		295	.90	1.80	200	520	62	162
" "		395	1.20	2.40	229	549	70	170
" "		495	1.50	3.00	247	567	77	177
Lead acetate	$Pb(C_2H_3O_2)_2$	96	.30	.60	47	367	15	115
" "	(325)	161	.50	1.00	67	387	21	121
" "		240	.74	1.48	108	428	34	134
Mercuric	$HgCl_2$	22	.80	.16	24	344	7	107
chloride	(271)	45	.167	.334	49	369	15	115
Bismuth tri-	$BiCl_3$	34	.11	.33	32	352	10	110
chloride	(316)	69	.22	.66	63	383	20	120
Potassium	KI	62	.40	.40	42	362	13	113
iodide	(166)	126	.80	.80	71	391	22	122
"		214	1.30	1.30	109	429	34	134
"		380	2.30	2.30	170	490	53	153
"		1,000	6.06	6.06	290	610	91	191
Sodium iodide	NaI	75	.50	.50	30	350	9	109
" "	(150)	125	.83	.83	56	376	18	118
" "		166	1.11	1.11	83	403	26	126
" "		250	1.67	1.67	109	429	34	134
" "		333	2.22	2.22	132	452	41	141
" "		400	2.67	2.67	158	478	49	149
" "		500	3.34	3.34	185	505	58	158
Cadmium	CdI_2	50	.14	.28	74	394	23	123
iodide	(366)	100	.28	.56	121	441	39	139
"		150	.41	.82	144	464	45	145
"		200	.54	1.08	168	488	52	152
"		250	.68	1.36	190	510	60	160
Cadmium	$CdCl_2$	66	.36	.72	38	358	12	112
chloride	(183)	150	.82	1.64	64	389	22	122
"		300	1.64	3.28	109	429	34	134
"		500	2.73	5.46	142	462	44	144
Barium chloride	$BaCl_2$	50	.24	.48	27	347	9	109
" "	(208)	150	.72	1.44	79	399	25	125
" "		300	1.44	2.88	133	453	41	141
" "		436	2.09	4.18	159	479	50	150
Copper chloride	$CuCl_2$	200	1.48	2.96	38	358	12	112
" "	(134)	300	2.24	4.48	60	380	19	119
" "		400	2.96	5.92	73	393	23	123
" "		500	3.68	7.36	83	403	27	127
" "		600	4.48	8.96	91	411	29	129
" "		900	6.72	13.44	125	445	39	139

TABLE III.—*Continued.*

Substance.	Chemical Formula.	Concentration.			Radiation Pb=1,000.		Radiation Water=100.	
		a	*b*	*c*	Salt Alone.	Total.	Salt Alone.	Total.
Calcium	$Cacl_2$	245	2.20	4.40	30	350	10	110
chloride	(111)	400	3.60	7.20	47	368	15	115
"		570	5.13	10.26	67	387	21	121
"		730	6.60	13.20	80	400	25	125
"		1,020	9.20	18.40	112	432	35	135
Sodium	Nacl	100	1.69	1.69	18	338	6	106
chloride	(59)	200	3.38	3.38	33	353	10	110
"		255	4.32	4.32	40	360	12	112
"		350	5.93	5.93	52	372	16	116
Ammonium	NH_4Cl	100	1.88	1.88	26	346	8	108
chloride	(53)	200	3.77	3.77	40	360	12	112
"		300	5.65	5.65	53	373	16	116
Potassium	K_2CO_3	100	.73	.37	26	346	8	108
carbonate	(138)	200	1.45	.73	40	360	12	112
"		300	2.18	1.09	50	370	15	115
"		400	2.90	1.45	58	378	18	118
"		600	4.36	2.18	66	386	21	121
"		900	6.54	3.27	91	411	29	129
Potassium	KOH	200	3.6	3.6	30	350	10	110
hydrate	(56)	420	7.5	7.5	63	383	20	120
"		720	12.8	12.8	80	400	25	125
Sodium	NaOH	200	5.0	5.0	12	332	4	104
hydrate	(40)	420	10.5	10.5	27	347	9	109
Zinc sulphate	$ZnSO_4$	140	.87	.87	25	345	8	108
" "	(161)	233	1.45	1.45	40	360	12	112
" "		350	2.16	3.50	54	374	17	117
Copper	$CuSO_4$	225	1.41	1.41	34	354	11	111
sulphate	(159)							

For those solutions which contain only atoms of low atomic weight the increase of radiation due to solution is nearly proportional to the concentration, even for high concentrations. In the case of solutions containing high atomic weight atoms the radiation is approximately proportional to the concentration for low concentrations, but as the concentrations increase the curves depart more and more from a straight line and seem to be approaching a limiting or saturating value. This is quite noticeable in the curves for lead nitrate and potassium iodide, which are very soluble in water.

If these results are plotted in terms of normal solutions on a

volume basis the curves approach even more to a straight line. For example, potassium iodide and copper chloride are so plotted in the dotted curves in Fig. 4. Copper chloride is now approximately a straight line. Now copper chloride in the solid form (Table II.) has a radiation of 180 in terms of water 100, and 140 for a concentration equal to 10 normal. The radiation of the solution is thus seen to be approaching very rapidly to the limiting value of the solid salt, which would seem to indicate that in solution the molecules may give more specific radiation than in the solid state.

When a salt contains an atom of high atomic weight it can be readily seen from the above results that the radiation is greatly increased, and, other things being equal, that the radiation follows the order of the atomic weight.

In order to bring this fact out clearly let us consider the bichlorides in the same manner as was done in the case of the powdered salts. The values for these are expressed in the following table.

Substance.	Molecular Weight.	Radiation for Concentration = 4.		Radiation (Atomic Wt.)$_2$.
		Total.	Total−Cl_2.	
Ba + Cl_2	137 + 71	50	43	.00228
Cd + "	112 + "	38	31	.00248
Cu + "	63 + "	17	10	.00252
Ca + "	40 + "	11	4	.00250
Hg + "	200 + "	X	105 (extrapolated)	.00262

In this table, the radiation for each salt is taken for equal concentration (in this case 4) and the radiation for pure water subtracted from it. The remaining radiation will be that due to the dissolved salt, less a small amount due to the water displaced.

It is readily seen from the figures in the fourth column of the above table that the radiation from the metal part of the salt increases very rapidly with the atomic weight of the metal. If this radiation is divided by the square of the atomic weights the result in each case is nearly a constant, as is shown in the last column. The greatest concentration obtainable with mercuric chloride was only .344 and therefore it cannot be compared directly with the others for a concentration of 4. I have however compared its radiation at

a concentration of .344 with that of barium chloride at the same concentration. From these two values the radiation of mercuric chloride at a concentration of 4 can be extrapolated and compared with the other bichlorides to a rough degree of approximation. This is shown in the last set of figures at the bottom of the table. The ratio of radiation divided by the square of the atomic weight in the case of mercuric chloride is thus in general agreement with the other chlorides. Whether this result is accidental, or really means something, cannot be decided with any degree of certainty as yet, but at any rate it can be definitely stated. I think that the radiation from the metal part of the salt (positive ion) does increase very rapidly with the atomic weight.

In the case of iodides the radiation also increases rapidly with the atomic weight of the positive ion; for a concentration = 1 the figures are, sodium iodide 22, potassium iodide 28, and cadmium iodide 52. In these the greater part of the radiation is undoubtedly due to the presence of the iodine. This fact can be shown by comparing the results for cadmium iodide and cadmium chloride. For equal molecular concentration both these salts contain the same amount of cadmium. The radiation for cadmium iodide for a concentration = 1.35 is 60, and for cadmium chloride for the same concentration, 19.

I have calculated the relative radiation due to the cadmium alone by taking the same proportional value as was used in the above table of bichlorides, and then subtracted this value from the total. The remainder in the case of cadmium chloride is 3.5, while for cadmium iodide it is 44.5. The ratio radiation/(atomic wt.)^2 for cadmium chloride is .00278, and for cadmium iodide .00276.

This interesting result is in agreement with that of the bichlorides and the ratio is of that same order.

We thus see that in all cases the presence of atoms of high atomic weight is responsible for a large radiation, and moreover, in a group of salts which have a common constituent of the same amount, the radiation due to the other constituent increases very rapidly with the atomic weight, being in the cases considered nearly proportional to the square.

If we have two salts which have a common constituent and the

other constituent in both of nearly the same atomic weight we would expect the radiations for equal concentrations to be practically the same. Copper sulphate and zinc sulphate are of this form, and we see from Table III. that for equal concentrations the radiations in the two cases are nearly equal, that of zinc sulphate being if anything a little greater. Copper sulphate could not be dissolved to a very high concentration, and therefore the figures for it are somewhat approximate.

For equal concentrations potassium hydrate gives a radiation which is much greater than that of sodium hydrate.

In the cases of lead nitrate the radical $(NO)_3$ seems to be a much more efficient radiator than the radical $(C_2H_3O_2)$, assuming that in each the lead gives the same amount of radiation.

The fact that in these salt solutions the various ions are in a very different degree of dissociation does not seem to have any influence on the general results.

Cane sugar, acetic acid, glycerine, and tartaric acid crystals, dissolved in water give very interesting results.

No change in the radiation from that of pure water could be detected for any concentration. Now cane-sugar and glycerine have a specific radiation the same as that of water, acetic acid a radiation slightly less, while tartaric acid was not measured, but is probably of the same order as water.

This result might be explained in the case of a liquid such as glycerine, acetic acid, by the fact that in any proportion whatever of the liquid and water the total number of parts of both kinds remains the same, and therefore also the total radiation, since the specific radiation in each is the same. In other words the increase of radiation due to the dissolved substance is just balanced by the decrease due to the solvent displaced.

This explanation however does not seem to fit in with the case of sugar and tartaric acid, as these substances are in the solid state to begin with, and when dissolved in water the number of both kinds in a given volume of the solution is continually increasing.

The molecular weights of sugar and water are widely different, and yet the radiations are the same, which shows that nothing can be based on mere molecular weights, even when these molecular

weights are made up of the same atoms. This fact will be brought out very clearly when we come to examine the results for the pure liquids in the next section.

Radiation from Pure Liquids.

For this series of experiments apparatus *B* was used in place of apparatus *A*. A preliminary set of readings for the radiation from metals was first tried to see how close the readings of one apparatus agreed with those of the other. The readings for the various metals by apparatus *B* relative to lead were always a little lower than by apparatus *A*. Aluminum, for example, gave with apparatus *B* a reading of 480 relative to lead as 1,000. The reading by apparatus *A* from Table I. is 500. The readings by apparatus *B* are therefore a little nearer to the true values for the secondary radiation, but the difference is not very great.

Over 50 liquids in all were tested, nearly all of them being organic. Over 20 of these were in sufficient quantity to test in the same cylindrical cell as was used for the aqueous solutions. The remainder of the liquids being very expensive and not present in the chemical department of the University in large quantities, a very much shallower cell had to be used. The surface of the liquid in this was the same as in the large cell but the depth was only 8 mm. The readings for the deep cell are therefore more correct than those for the shallow cell. Whenever possible readings were made with the liquid in both cells.

The observations were made in exactly the same manner as in case of the aqueous solutions of the salts. Pure water was taken as the standard and its radiation put equal to 100, the other liquids being calculated in terms of it. On this same scale the radiation for lead was 340 for the deep cell and 360 for the shallow one.

The results for all the liquids tested are shown in Table IV. The first column represents the name of the liquid these being arranged according to their chemical grouping. The second column gives the chemical formulæ of the liquids. The third column expresses the molecular weights, and the fourth the densities. In the fifth column are placed the values for the secondary radiation from the liquids using the deep cell, and in the sixth column the same using the shallow cell.

TABLE IV.

Liquid.	Chemical Formula.	Molecular Wt.	Density.	Secondary Radiation Water = 100.		Relative Absorption of β Rays Water = 100.
				Thick Layer.	Thin Layer.	
Water Group—						
Water	H_2O	18	1.000	100	100	100
Methyl alcohol	CH_3OH	32	.790	74	80	70
Ethyl "	C_2H_5OH	46	.800	74	80	70
Amyl "	$C_5H_{11}OH$	88	.812	74	80	70
Allyl "	C_3H_5OH	58	.858	125	—	—
Tertiary butyl alcohol	C_4H_9OH	74	.786		78	70
Iso " "	C_4H_9OH	74	.803		77	74
Ether	$(C_2H_5)_2OH$	74	.736	75	—	—
Acetic anhydride	$(C_2H_3O)_2OH$	102	1.073	74	—	74
Acid Group—						
Formic acid	CH_2O_2	46	1.227	131	—	—
Acetic "	$C_2H_4O_2$	60	1.057	89	—	87
Valeric "	$C_4H_9(COOH)$	102	.958	122	—	—
Propionic acid	$C_3H_5(CO_2H)$	74	.996	—	81	100
Butyric "	$C_3H_7(CO_2H)$	88	.962	—	81	100
Caprylic "	$C_7H_{15}(CO_2H)$	144	.929	—	81	80
Ester Group—						
Amyl ester	$CH_3(CO_2C_5H_{11})$	130	.857	75	—	—
Formic "	$H(CO_2C_2H_5)$	74	.936	—	77	62
Acetic "	$CH_3(CO_2C_2H_5)$	88	.905	—	77	70
Propionic ester	$C_2H_5(CO_2C_2H_5)$	102	—	—	77	70
Methyl acetate	$CH_3CO_2CH_3$	74	.956	—	77	71
Iso butyric ester	$C_4H_9COOC_2H_5$	116	.890	—	77	80
Hydrocarbons—						
Benzene	C_6H_6	78	.879	74	—	70
Toluene	$C_6H_5CH_3$	92	.822	74	—	70
Ethyl benzene	$C_6H_5C_2H_5$	106	.866	—	80	86
Amylene	C_5H_{10}	70	—	—	71	45
Halide Group—						
Methyl iodide	CH_3I	142	2.199	280	329	285
Ethyl "	C_2H_5I	156	1.944	—	326	295
Amyl bromide	$C_7H_{11}Br$	151	1.543	170	197	175
Brom benzene	C_6H_5Br	157	1.495	198	196	196
Chlor "	C_6H_5Cl	113	1.106	100	—	101
Propyl chloride	C_3H_7Cl	79	.916	—	80	65
" bromide	C_3H_7Br	123	—	—	230	141
Tertiary butyl bromide	C_4H_9Br	137	—	—	189	118
Iso amyl "	$C_5H_{11}Br$	151	1.666	—	276	280
Iod benzene	C_6H_5I	204	1.833	—	294	330

TABLE IV. —*Continued.*

Liquid.	Chemical Formula.	Molecular Wt.	Density.	Secondary Radiation Water = 100.		Relative Absorption of β Rays Water = 100.
				Thick Layer.	Thin Layer.	
Halide Group—						
Ethylene chloride	$C_2H_4Cl_2$	99	1.280	—	284	400
" bromide	$C_2H_4Br_2$	188	2.178	—	245	140
Chloroform	$CHCl_3$	119	1.526	172	190	175
Carbon tetrachloride	CCl_4	154	1.630	172	190	175
Tetra brom acetelene	C_2Br_4	344		—	290	560
Amine Group—						
Aniline	$C_6H_5NH_2$	93	1.022	74	—	88
Methyl aniline	$C_6H_4NHCH_3$	107	.976	79	—	88
Di methyl aniline	$C_6H_4N(CH_3)_2$	121	.955	78	80	—
Ortho chlor aniline	$C_6H_4NH_2Cl$	128	1.234	101	—	100
Meta chlor aniline	$C_6H_4NH_2Cl$	128	1.243	103	—	100
Mono ethyl "	$C_6H_5NHC_2H_5$	121	.951	—	77	88
Meta brom "	$C_6H_4NH_2Br$	172	—	—	189	230
Di methyl toluidine	$C_6H_4CH_3N(CH_3)_2$		—	—	77	88
" " amine	$(CH_3)_2NH$	45	—	—	77	71
Ortho toluidine	$C_6H_4CH_3NH_2$	107	1.003	—	77	—

Let us now examine these results in detail taking them by groups.

Water Group. — In this group besides water we have a number of alcohols, ether, and acetic anhydride. The secondary radiation from these, with the exception of allyl alcohol, is the same and about 25 per cent. less than that of water. The results for the shallow cell, as can be seen from the table, give values, which are higher relatively to water than those for the deep cell. This result is common to all the liquids and is probably caused by the different arrangement of the liquid in the two cases. It is, however, seen that if two liquids have the same radiation in one cell they also have equal radiation in the other, and therefore comparisons can be made of the various liquids without introducing any appreciable error. In fact one can calculate very approximately from the values obtained by the shallow cell what the radiation would be from the deep cell.

In this group water has a much larger value than one would expect judging by the atomic weight of its atoms. The hydrogen atoms cannot of themselves give a very great radiation, at least on

any atomic hypothesis of secondary radiation, and the large radiation given by water must therefore be due to the oxygen atoms, or to a special arrangement of these atoms.

Acetic anhydride has a much greater molecular weight than water, and contains more atoms of higher atomic weight, and yet the radiation from it is much less than that of water. We see at once from this that the molecular weight of the molecules of the liquid has in general no deciding effect on the amount of radiation given off. Even the substitution of an atom of higher atomic weight does not always result in a higher radiation, though it does in general, other things being equal.

This very interesting phenomenon will be much more markedly brought out in some of the other groups.

Density of the liquid does not have any apparent effect in general on the radiation, the density of acetic anhydride for example being greater than that of the water.

Allyl alcohol forms a remarkable exception on this group giving a radiation which is 25 per cent. greater than that of water and 66 per cent. greater than that of the other alcohols. Its molecular weight is less for example than that of amyl alcohol, it has a smaller number of carbon and hydrogen atoms, and yet a much greater radiation. What is the cause then of this anomalous result? Allyl alcohol has what chemists term a double bonding of the carbon atoms and this may have some very marked effect on the secondary radiation. This is the first indication I know of that the interatomic relations can have any effect on the secondary radiation, the phenomena being due, according to the present theories, to a subatomic action. Before discussing this further it will be better I think to examine the other groups.

Acid Group. — In this group are a number of organic acids. Propionic, butyric and caprylic acids show nothing unusual and have about the same radiation as the alcohols, though the number of atoms differ largely. Acetic acid has a higher radiation than alcohol, but still not quite as great as water.

The two great exceptions occur in the case of valeric and formic acids, the radiation in these exceeding that of water by a considerable amount. Formic acid which has the greatest radiation has

the least number of atoms. In this group also the chemical arrangement of the molecules must have a considerable effect on the radiation.

Ester Group. — The esters all have about the same radiation as alcohol, and show no unusual features. Here again the molecular weights vary between wide limits without causing any change in the radiation.

Hydrocarbons. — Benzene, toluene, nitro benzene and ethyl benzene have the same radiation as alcohol. Here we have a very simple arrangement of the carbon and hydrogen atoms, and yet the radiation is the same as for the more complicated. The addition of a number of oxygen atoms to the carbon and hydrogen does not therefore in many cases add any more radiation.

Amylene is an exception to this group and its radiation is the lowest of any of the liquids yet examined, the value being about 65 in terms of water 100.

Amine Group. — This consists for the most part of aniline and its various derivatives of the form of ammonia compounds. Aniline methyl aniline, dimethyl aniline, mono ethyl aniline, dimethyl, toluidine, dimethyl amine and ortho toluidine have all the same radiation as alcohol. The presence of a nitrogen atom has apparently not changed the amount of the radiation.

Ortho chlor aniline and meta chlor aniline have a greater radiation than that of alcohol, being about the same as water. This increased radiation is probably caused by the presence of the chlorine.

Meta brom aniline shows very clearly by its large increased radiation the presence of the bromine atom.

Its radiation is over double that of aniline.

One atom then of high atomic weight may be in many cases of more importance in producing secondary radiation than a greater number of atoms of lower atomic weight.

Halide Group. — This is the most interesting group of all, and includes those liquids which contain the highest atomic weight atoms and have the greatest density. The liquids are all compounds of carbon and hydrogen in various proportions, and chlorine, bromine and iodine.

In general, as can be seen from the values given in the tables,

the radiation follows the orders of the atomic weight of the chlorine, bromine and iodine constituents, but these are several remarkable exceptions.

Let us consider first those which contain chlorine. Propyl chloride has the lowest radiation of any, about the same as alcohol. Chlor benzene is next in order, having a radiation about the same as water. Both these contain the same number of chlorine atoms and their only difference is in the amount of carbon present.

Chloroform and carbon tetrachloride have the same radiation, which is nearly double that of water. The adding of ∞ chlorine atoms does not always make a difference in the radiation.

Ethylene chloride is the most remarkable one in this group, the radiation being nearly three times as great as water. Comparing it with propyl chloride we see that the amount of carbon and hydrogen is less and the chlorine just double. At first sight we might think that the increased radiation is due to the extra amount of chlorine present, but then chloroform and carbon tetrachloride contain even more chlorine and have a yet smaller radiation. The large radiation cannot therefore be due entirely to the chlorine, and it certainly is not caused by the carbon and hydrogen.

Before discussing this exception further let us look at the results for the iodides and bromides. The three iodides, ethyl, methyl and benzene, all have a very high radiation, the greatest yet measured for any liquid. Methyl iodide has the largest radiation of the three, being over 90 per cent. that of lead, and greater than the value of antimony in Table I. In fact, if we consider that the radiation here is almost entirely due to the iodine present, the value of this radiation will fall very close to that for pure iodine from Table I. These three liquids contain each the same amount of iodine and exhibit no anomalous effects.

The radiation from the bromides is intermediate in value between that of the chlorides and that of the iodides, though tetra brom acetelene has almost as great a value as iod benzene. The results for the bromides are almost as irregular as those for the chlorides. In no case, however, is the radiation very low.

Comparing propyl bromide with propyl chloride, we see that the radiation in the case of the former is nearly three times as great as

that of the latter. In both the carbon and hydrogen is the same, but the substitution of a bromine atom for a chlorine one causes the radiation to increase very rapidly. On the other hand ethylene bromide has a smaller radiation than ethylene chloride. Here the effect of substituting the bromine for the chlorine is to decrease the radiation.

This remarkable and totally unexpected result, together with the others of similar nature, in this and the other groups, lead very clearly I think to the conclusion that there is present in some of these liquids phenomenona which to a great extent control the secondary radiation, and which cannot be explained entirely on any simple atomic theory. It seems more likely to depend to a large extent on the molecular arrangement of the constituent parts of the liquids. Hitherto we have been accustomed to consider the secondary radiation as being controlled entirely by the atom of the bombarded substance, but in view of the above results we are forced to conclude that the molecule or groups of associated molecules have also very large influences. Many of the above liquids are believed by chemists, from experiments on the freezing and boiling points, to be in a state of a molecular association, but unfortunately no definite information can be had which is of much use to the physicist. Therefore nothing definite can be said of the association of those liquids in Table V. which show anomalous effects. It is difficult for me to see how they can be explained entirely on any subatomic theory such as has been advanced hitherto.

TABLE V.

Substance.	Radiation in Per Cent.			
	Uncovered.	.0011 cm. Foil.	.0021 cm. Foil.	.0043 cm. Foil.
Lead	100	77	60	35
Copper	100	75	59	34
Carbon	100	73	54	—
Chloroform	100	—	68	40
Water	100	—	70	42
Benzene	100	—	70	47
Lead nitrate	100		67	36
Potassium iodide	100		66	37
Copper chloride	100		69	39

It must not be forgotten that in this entire research only one angle of incidence of the primary rays has been used. It is possible that like McClelland's results for metals,[1] there is present in the total secondary radiation from liquids two constituents varying in individual values with the angle of incidence. One of these constituents might depend entirely upon the atomic weight of the atoms, while the other would be independent of atomic weight but be controlled by molecular arrangement.

In the author's experimental arrangement the latter constituent might be at a maximum, and in some liquids mark or overcome the other.

Before this point can be considered with any degree of certainty experiments at different angles of incidence will have to be made. It is the intention of the author to carry these out as soon as possible.

I do not think, however, that the angle of incidence will be able to account entirely for such an extreme change as takes place in the ethylene chloride.

In looking over the results in the above table one is struck with the great number of compounds of carbon, hydrogen, oxygen and nitrogen in all proportions which has the same radiation. The only exceptions observed are allyl alcohol, formic and valeric acids. In most cases then the radiation from a liquid composed of carbon, hydrogen, oxygen and nitrogen is independent of the number of atoms present, and has a constant value, about .75 per cent. of that of water.

ABSORPTION OF THE SECONDARY RAYS BY TINFOIL.

In order to determine whether the secondary rays from solids, solutions and pure liquids differed much in velocity, a short series of tests on their absorption by tinfoil were made.

Apparatus *B* was used in the same manner as already described. Sheets of tinfoil were interposed in the path of the rays and the decreased ionization measured. From these values, and the reading without any tinfoil, the absorption in per cent. was calculated in the usual manner. The values so obtained will serve very well to compare the average penetrating power of the different rays.

[1] *Loc. cit.*

The results are expressed in Table V. The values for the three metals — lead, copper and carbon — are of the same nature as obtained by apparatus *A*, the penetrating power of the rays decreasing slowly with decrease in atomic weight.

In the case of pure liquids the results are quite different, the penetrating power of the rays not differing much for the three liquids observed and being in all cases greater that that of the metals. The velocity of the rays from pure liquids thus seems to be on the average greater than from pure metals, and the lighter the atom is the greater is this velocity, though the difference is very small.

The solutions — lead nitrate, potassium iodide and copper chloride — show similar results to the liquids, though not quite to so marked an extent.

Since the velocities of the rays from the various liquids and solutions do not apparently differ very much in value, the readings which have been obtained for the secondary radiations from these will represent more nearly the real values than is the case for the pure metals.

The fact that the penetrating power of the rays from liquids is greater than for those from the pure metals is difficult to explain on the disintegration theory of the atom.

Absorption of the β Rays by Pure Liquids.

If the second radiation from liquids is due to a scattering of the primary beam, then the difference between the total incident radiation and the total transmitted radiation will represent the total absorption. This absorption will be made up of two parts, the true absorption of the rays in the liquid and the scattered radiation which gets turned completely back and appears on the incident side as so-called secondary radiation.

Whatever the mechanism of the liquid which affects the secondary radiation, the same mechanism should affect the absorption in the same degree. There ought therefore to be a definite relation between the amount of secondary radiation from a given liquid and the absorption of the primary rays by the same liquid.

It was therefore of the greatest interest to see if those liquids

which showed remarkable radiating power would also exhibit anomalous results for the absorption of the primary rays.

The accessory apparatus used for this experiment is shown in Fig. 2, and may be briefly described as follows:

The absorption cell consists of a thick block of lead (*a*) in the center of which a hole (*b*) is drilled. A glass tube with carefully ground ends fits closely in this hole. The length of the tube is slightly greater than the thickness of the lead block. On the top of the glass tube rests a washer of lead, and over this a brass plate *C*. There is the same arrangement at the bottom of the tube, and the two brass plates *C* and *d* are firmly pressed together by screw bolts. Between the bottom of the tube and the lead washer is placed a thin mica sheet. This arrangement makes a very liquid tight joint.

The tube of radium *R* is placed beneath the opening in the lower plate *d*, which is made small so as to confine the β rays to a fairly narrow beam.

The cell is placed directly underneath the ionization chamber of apparatus *B*.

In making an absorption test of any liquid the standard of the electrometer was always set at a definite position for which the ionization was considerably less than that due to the β rays. The liquid under test was then poured into the cell by means of a fine capillary pipette and the level carefully adjusted until the ionization due to the β rays was cut down to the same value as that of the fixed position of the standard. The initial reading for every liquid was therefore the same. This procedure insured that in every liquid we were concerned with the same quantity of rays initially, and also that these rays were of the same average velocity. Moreover, the disturbances due to the capillary action and non-uniformity of the thickness of the initial layer were thus eliminated.

Each liquid in this way was tested under exactly the same conditions, and therefore any error due to difference in velocities would be the same for all.

After this reading was obtained a known quantity of the liquid was poured into the cell and the new ionization measured. The shape of the meniscus in both cases would be the same, and there-

fore the pouring in of a known quantity of liquid would mean a known increase in thickness of the liquid.

The beam of β rays was quite small in area at the bottom of the cell and therefore passed almost entirely through the center of the meniscus.

The results for a number of liquids are shown plotted in the curves of Fig. 5, the ordinates representing the ionization and the abscissæ the thickness of absorbing layer in mm.

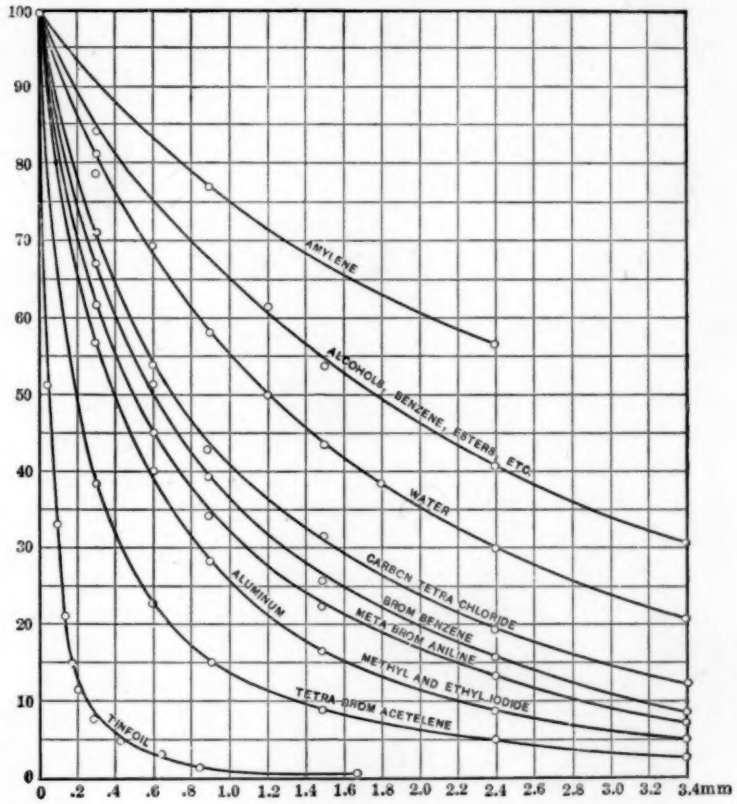


Fig. 5.

The relative absorbing power of these liquids was compared in the following manner: Water was taken as the standard and the thickness of water necessary to cut down the radiation to a definite amount (*e. g.*, 50 per cent.) was put equal to 100. The thickness necessary to reduce the radiation to the same amount for any other

liquid was then read off from the curves and expressed in terms of water 100.

By an examination of curves it is seen that this ratio is nearly constant throughout a large portion of the curves, especially for the low absorption ones.

The average values over a considerable range were taken for the various liquids and are placed in the last column of Table IV., where they can be conveniently compared with the relative secondary radiations for the same liquids.

A number of these liquids were so volatile that it was difficult to obtain a very correct reading as the thickness of the liquid would change before the electrometer could be balanced.

In such case the relative absorption as taken from curves is too low.

Looking through this last column we see a remarkable parallelism between the relative secondary radiation from a liquid and its relative absorption. Those liquids which have a radiation less than water have in nearly all cases an absorption less than that of water, while those which have a high radiation have, with a few exceptions, also a high absorption. Those compounds of carbon, hydrogen and nitrogen which have a nearly constant radiation, give a relative absorption, which, considering the errors of observation, is also quite close to a constant.

Amylene, which gave the lowest radiation, shows the smallest amount of absorption, though the value obtained is, on account of the great volatility of the liquid, abnormally low.

In the group of halides there is, with two or three exceptions, very good agreement between the radiation and absorption. Those liquids which show anomalous results for the secondary radiation exhibit the same for the absorption of the primary rays. Propyl chloride is much less than propyl bromide, while ethylene chloride is much greater than ethylene bromide, the same as was the case for the secondary radiation. Chloroform and carbon tetrachloride have the same radiation and also about the same absorption. Tetra brom acetelene shows a very high absorption, much greater than one might expect from its radiation, though this is high also.

We thus see, from these tests on the relative absorption of the primary rays by the liquids, that there is an intimate relation in most cases between the secondary radiation and the absorption. What-

ever mechanism of the liquid is responsible for the production of secondary radiation, that same mechanism must affect the absorbing powers in the same way.

It can be seen from Table IV. that the absorption is in no way dependent on the density of the liquid, though as a general rule those liquids which have a high density have also a high absorption.

N. Campbell has very recently published a paper[1] on the absorption of β rays of uranium by liquids. He examines water, alcohol, aniline, liquid paraffine and aqueous solutions of NaI, KNO_3 and K_2CO_3, using a thick piece of filter paper to hold the liquids. The absorption curves which for solids are exponential, show for liquids great irregularities, and no definite conclusions for them can be deduced. At any rate it is evident from his results that λ/ρ is not a constant for liquids (λ being the absorption coefficient and ρ the density).

The filter paper method of examining the radiating and absorbing power of liquids and solutions seems to me open to objections on account of the non-homogeneity of both thickness and material.

The absorption curves given by the author for liquids are not exponential, but the rays in this case are not homogeneous, as would be the case for uranium.

The absorption curves for tinfoil, aluminum, silver and platinum were also taken at the same time and under exactly the same conditions as those for the liquids. The curves for aluminum and tinfoil are plotted in Fig. 5. Aluminum happens to coincide with the curve for methyl and ethyl iodide, which shows that the absorption of aluminum is the same as that for the iodides. The atomic weights of the atoms are, however, in the two cases entirely different.

The radiation of aluminum is very much lower than that of the iodides.

The solids then are more efficient absorbers than the liquids for equal atomic weights, but the same is not true with regard to radiation.

Absorption of γ Rays by Liquids.

A short series of tests on the absorption of γ rays by liquids was made. The radium was covered with a sheet of lead of sufficient

[1] Phil. Mag., January, 1909.

thickness to cut out all the β rays. A cylindrical glass vessel was used to hold the liquids and was large enough in diameter to include all rays which could possibly enter the ionization chamber.

The rays here used are of the soft kind and are clearly not homogeneous.

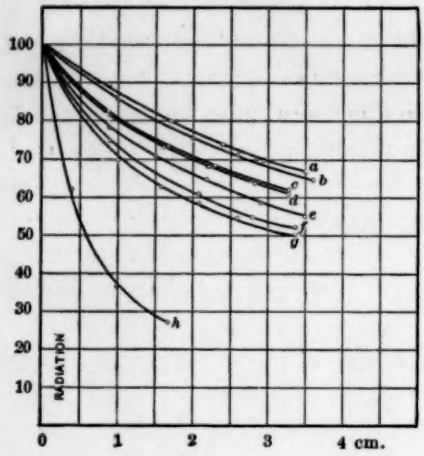


Fig. 6.

The results obtained are shown in Fig. 6, where the ordinates represent radiation, and the abscissæ the thickness of the liquid. Curve *a* is that for water, alcohol, benzene and acetic acid, which all have about the same absorbing power.

Curve *b* is that for nitro benzene and glycerine; curve *c* that for chloroform; curve *d* that for carbon tetrachloride; curve *e* brom benzene; curve *f* ethyl iodide; and curve *g* that for methyl iodide. Curve *h* represents the absorption in the case of mercury.

The absorption of the γ rays by liquids follows in general the order of the atomic weight of the heaviest atom. The density of the liquid seems however in certain cases to have a large effect. In those liquids of low density the absorption is nearly the same.

Mercury is very much greater in absorbing power than any of the rest. Its atomic weight and density are also much greater.

CONCLUSION.

It is not the intention of the author in this present paper to advance any new theory of secondary radiation, or to reconcile the

facts therein described with the present theories. The results here stated, especially those with regard to the pure liquids, are entirely too complicated and anomalous to be satisfied with any simple theory of atomic disintegration, and a great deal more work will have to be done on the subject before the true explanation is arrived at.

Although in a great many cases the secondary radiation does seem to be a function of the atomic weight, yet there are, as has been shown, many exceptions which are undoubtedly in some way closely associated with the way in which the atoms are combined with one another chemically. The arrangement of the molecules is in all probability a very important factor in the production of secondary radiation from pure liquids.

At any rate it is too early yet to put forward any hypothesis to account for the author's results, even if a logical one were at hand.

We are perhaps too liable at the present time to advance incomplete and illogical theories, and it is an open question whether our true scientific knowledge is increased by such a procedure, if indeed we do not in many cases delay the truth.

As can be readily seen by a careful consideration of this paper, there are a great many interesting points brought up which need further investigation, and it is the intention of the author to take them up as soon as convenient in the hope that more light may be thrown on the abnormal results here described.

The secondary radiation from various substances is of the greatest importance in deciding whether or no the atoms can be disintegrated by outside agency.

The present research, while not deciding this question, certainly shows that the process is not in general simple, and in a great many cases that there are other very important factors coming in besides the atoms.

In conclusion I wish to express my obligation to Professors Jones and Fry of the chemical department of the University, for placing at my disposal the many expensive chemicals used in this research, and for valuable chemical advice. The research has also been greatly aided by apparatus and supplies purchased by a grant from the Bache fund of the National Academy of Sciences.

UNIVERSITY OF CINCINNATI,
April, 1909.

ON THE PHOTOELECTRIC EFFECT OF SODIUM-POTASSIUM ALLOY AND ITS BEARING ON THE STRUCTURE OF THE ETHER.

BY JAKOB KUNZ.

THE velocity of electrons emitted by a plate of metal exposed to ultra-violet light or Roentgen rays does not depend upon the intensity of the light; while the number of electrons emitted per unit time from unit surface increases with the intensity of the rays. This fact seems to indicate that the forces which expel the electrons from the metal are not the electric forces in the light wave incident on the metal; but that the electrons are expelled by a kind of explosion of some molecules of the metal, which under the action of the light, have become unstable in their equilibrium. If this view of the nature of the photoelectric effect were right the velocity of the electrons emitted would not at all depend on the light applied but would be determined by the properties of the atom of the metal. For each metal there would be a characteristic velocity with which the electrons escape; and one special wave-length or a small interval of wave-lengths would be required to produce the explosion in the same way as, for instance, a particular wave-length of light is required to excite the explosive decomposition of the compound NBr_3.

The mechanism of the photoelectric effect might also be similar to a process of resonance. The incident light sets the electrons of the metal into forced vibrations, the amplitude of which may become so large that the electron is emitted from the atom with a certain velocity characteristic for each element; the nearer the period of the incident light is to that of the free vibrations of the electrons, the greater will be the amplitude of the forced vibrations; and when a given value of the amplitude has been reached the electron will be shot out of the atom. In this case of resonance again one special wave-length would produce a maximum velocity of the electrons,

while the velocity of electrons emitted under the action of light of smaller or greater wave-length would decrease very rapidly. Some experiments made by E. Ladenburg[1] make the theory of explosion or of simple resonance improbable. E. Ladenburg found that the velocity of electrons emitted from plates of platinum, copper and zinc, under the action of ultra-violet light of wave-lengths from 270–220 $\mu\mu$, increases proportionally to the frequency of the light. It may be shown, however, that the numbers obtained by E. Ladenburg agree with the assumption that the square of the velocity is proportional to the frequency. However this may be, the velocity of the electrons is independent of the intensity of the light and depends only and in a continuous way on the wave-length of ultra-violet light. This would be very improbable if the electrons were expelled by an explosion of the atoms. It is more probable that the kinetic energy of the electrons emitted is transformed energy of radiation of the incident light, and yet as we have seen, the kinetic energy is independent of the intensity of the light. How can these two facts be reconciled?

Sir J. J. Thomson[2] pointed out a long time ago that the small fraction of the molecules of a gas ionized by Roentgen rays and ultra-violet light suggests that these rays possess a structure. The electromagnetic energy in these rays is localized in special regions and the great majority of the molecules of the gas are not ionized because they are not struck by those regions of intense electric and magnetic forces. The front of the electromagnetic disturbance in a Roentgen pulse is not a surface of uniform illumination, but resembles rather a series of bright specks on a dark background. The same conclusion may be drawn with regard to the ultra-violet light producing ionization in a gas or the emission of electrons from metal surfaces. The structure in the wave front implies that the ether through which light is travelling has also a structure.

According to Maxwell's theory of electrodynamics, the distribution of the energy in the electric, magnetic and electromagnetic field is continuous. The lines of force are a mere mathematical

[1] Erich Ladenburg, Physikalische Zeitschrift, 8, p. 590, 1907; 9, p. 821, 1908.

[2] J. J. Thomson, "On the Ionization of Gases by Ultra-violet Light and on the Evidence as to the Structure of Light Afforded by its Electrical Effects," Proceedings of the Cambridge Philosophical Society, Vol. XIV., Pt. IV., p. 41 f., 1908.

fiction. Faraday, however, attributed to the tubes of force some physical meaning. The properties of the ether inside and outside the tubes are different and the electric energy is localized along these tubes while the space free of tubes contains no energy. Thus in a charged condenser the energy is localized along the individual lines of force in a discontinuous way (see Fig. 1). Let us suppose also that the number of Faraday tubes connected with the electron is a limited one. If the electron that was moving with a velocity v, comes into collision with a solid obstacle, each individual tube will be disturbed during the time of collision τ and the disturbance consisting in a tangential electric force T in the direction PQ of Fig. 2, and a new magnetic force perpendicular on the plane OPQ will travel out in the direction OPP' with the velocity of light; t seconds after the electron began to be stopped, the disturbance of the tubes will be found in the shell of thickness δ between two spheres and the total amount of energy in the Roentgen pulse will be equal to

Fig. 1.

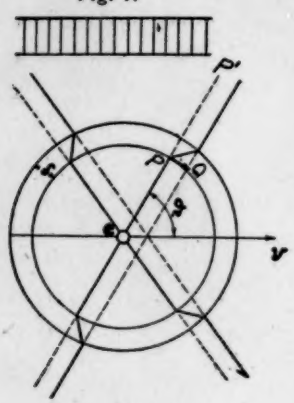


Fig. 2.

$$E = \frac{2}{3}\frac{e^2v^2}{\delta}.$$

This energy is spread continuously through the shell with variable density according to ordinary electrodynamics, while it is localized in a certain number n of isolated bundles of intense electric and magnetic forces, the average energy of such a region would be $\frac{2}{3}\cdot e^2v^2/\delta n$. Thus the front of the disturbance corresponding to the Roentgen rays is not a surface of uniform electromagnetic illumination, but resembles rather a series of bright specks on a dark background. The energy appears to be divided up into units of invariable character. If in the old emission theory of Newton we replace the moving particles by isolated Faraday tubes set in vibration we get a picture of this new form of the theory of light.

This structure of light or the distribution of the electromagnetic

energy in distinct units would just account for the facts that the number of the molecules of a gas when struck by Roentgen rays is exceedingly small and that the velocity of the electrons emitted from metals under the action of Roentgen rays and ultra-violet light is independent of the intensity of the light, that the velocity increases with decreasing thickness δ of the Roentgen pulse and that the number of electrons emitted from unit surface in unit time increases with increasing number of units of electromagnetic energy passing the same surface in the same time, or the number of electrons emitted from a metal must increase with the intensity of the Roentgen rays and the ultra-violet light. Indeed, if a unit of electromagnetic energy colliding with a molecule can at any place make it liberate an electron it will do so, and start the electron with the same velocity, whatever may be the distance from the source when the unit impinges on a molecule. Thus the velocity would be independent of the intensity of the light. A given source of Roentgen rays, or of ultra-violet light, emits per unit time a certain number of units; the fraction of these units passing through unit surface at a certain distance from the source will be inversely proportional to the square of the distance; the further we recede from the source the smaller the number of units passing through unit surface, and therefore the smaller the number of electrons emitted from the metal.

According to the electron theory of radiation, the waves of heat and light emitted by a hot black body is of the same origin as the Roentgen radiation. The electrons like an exceedingly thin gas come into collision with the molecules of the substance and produce Roentgen pulses. The electromagnetic disturbance in the pulse can be resolved into simple harmonic vibrations by means of Fourier's theorem. And when such a disturbance goes through a prism the elementary oscillators resolve according to their own period of vibration the pulse arriving in the beam of light.

The thickness δ of the pulse is equal to $\delta = c\tau$, where τ is the time of collision between an electron and an atom and c is the velocity of light. In order to account for the laws of radiation we have to admit that the time of collision τ is inversely proportional to the square of the velocity of the electron or inversely proportional to the absolute temperature of the body. If c_1 is a propor-

tionality factor, we have

$$\tau = \frac{c_1}{v^2},$$

hence

$$\delta = \frac{cc_1}{v^2} = \frac{c_2}{v^2},$$

$$E = \frac{2}{3}\frac{e^2v^2}{\delta} = \frac{2}{3}\frac{e^2v^4}{c_2},$$

or

$$E = \frac{2}{3}\frac{e^2c_2}{\delta^2}.$$

The energy in a Roentgen pulse is proportional to the fourth power of the velocity of the electron. It would be important to test this relation. From the last equation we see that the energy in the pulse is inversely proportional to the square of the thickness of the pulse. Thin pulses will have more energy than broad pulses. Therefore we should expect that the velocity of electrons produced by hard rays is greater than that of electrons produced by soft Roentgen pulses. This conclusion agrees with the results of experiments.

When a Roentgen pulse passes over an atom containing electrons, the electrons will be acted upon for a very short time by a strong electric force. The electrons will be subject to a very strong acceleration and will emit secondary Roentgen pulses of a certain thickness δ_2. If the forces between the electron and the rest of the atom are weak the electron may be ejected, accompanied by a secondary pulse. If these forces between the electron and the atom are strong the electrons after the displacement by the pulse may vibrate through their positions of equilibrium and produce disturbances of a periodic character or ordinary light. The first process constitutes the ejection of electrons and the production of secondary Roentgen radiation, while the second process gives rise to the phenomena of phosphorescence.

As the energy in each pulse is inversely proportional to the square of the thickness, we conclude that the thickness of the secondary pulse cannot be less than that of the primary radiation.

If E_1 and E_2 represent the energy in the primary and secondary radiation and δ_1 and δ_2 the thickness of the pulses, we have

$$E_1 \geqq E_2,$$
$$\delta_1 \leqq \delta_2.$$

This agrees with the results of experiments made by Barkla on secondary radiation. The rule derived in this way corresponds exactly to Stockes' rule of phosphorescence, when we replace the thickness of the Roentgen pulse by the wave-length of light.

$$\frac{cc_1}{v_2} = \delta = \frac{c_2}{T},$$

where T represents the absolute temperature of the radiating substance. Now the velocity of the electrons in the discharge tube is much larger than the velocity of the electrons in a metal at ordinary temperature; the pulses from metals at ordinary temperature and even at high temperature will therefore be much thicker than the electromagnetic pulses emitted from a Roentgen tube. The energy in the disturbance that constitutes ordinary light will be smaller than the energy contained in the Roentgen pulses themselves, and we should therefore expect that the velocity of the electrons emitted from metals struck by Roentgen rays is far greater than the velocities of the electrons produced by the impact of ultra-violet light. Indeed, the velocity of the electrons emitted under the action of Roentgen rays is of the order of magnitude 10^{10} cm./sec., while the velocity of those emitted by ultra-violet light is less than 10^8 cm./sec.

Let us suppose that an electron comes at O of Fig. 3 into collision with an atom, and that its velocity falls from its constant value v to zero, during the time interval $\tau/2$. The Faraday tube t seconds after the beginning of the collision will have the position $OP_1P_2P_5$. If, however, the electron begins to move immediately after the stoppage in the opposite direction along the same line as before, and if during the next interval $\tau/2$ it acquires its original velocity v again, then the shape of the Faraday tube t seconds after the beginning of the accident will have the form $O_1P_2P_3P_4$. There will be a tangential component of the electric force $P_1Q_1 = P$ of given direction in the point P_1 and in all points along the line P_1Q_2 and the same tangen-

tial component of opposite direction in the point Q_2 and along the line Q_2P_3. The constitution of the pulse represented by the two parallelograms $P_1A_1A_2Q_2$ and $Q_2P_3A_4A_3$ of Fig. 4 is now more complicated than it was before, and we see from Fig. 4 that half of the thickness of the pulse corresponds to half a wave-length of light, or the thickness δ of the complicated Roentgen pulse due to the type of collision as it occurs in the metals, will correspond to a

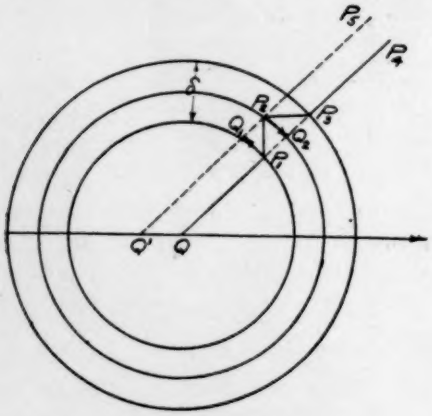


Fig. 3.

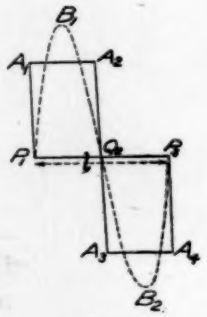


Fig. 4.

wave-length λ of ordinary light. The energy in the pulse is inversely proportional to the square of the thickness of the pulse; from the analogy drawn between the two processes we should expect that the energy of a light wave will be inversely proportional to the square of the wave-length λ of the light.

If in the case of a collision the velocity of an electron instead of being reduced to zero is diminished by dv during the interval dt we find that the magnetic force H in the corresponding pulse is equal to

$$H = \frac{e}{c}\frac{dv}{dt}\frac{\sin\vartheta}{r}$$

and the tangential electric force T is equal to

$$T = \frac{e}{c^2}\frac{dv}{dt}\frac{\sin\vartheta}{r}.$$

But the acceleration f of the electron is equal to

$$f = -\frac{dv}{dt},$$

hence

$$H = -\frac{ef}{c}\frac{\sin\vartheta}{r},$$

$$T = -\frac{ef}{c^2}\frac{\sin\vartheta}{r},$$

and the energy dE emitted from the electron during dt will be given by the expression

$$dE = \frac{2}{3}\frac{e^2f^2}{c}dt.$$

Let us suppose that during a collision the velocity of the electron changes according to

$$v = v_0 \cos(2\pi nt),$$

that τ is the interval of time of a collision, where the velocity changes from v_0 to o and to $-v_0$, and that $n\tau = 1$, then we have

$$f = -\frac{dv}{dt} = v_0 2\pi n \sin(2\pi nt).$$

The energy radiated away from the electron during the time τ of a collision will be equal to

$$E = \frac{2}{3}\frac{e^2}{c}v_0^2\pi^2n^2\int^{\tau}\sin^2(2\pi nt)dt,$$

$$= \frac{2}{3}\frac{e^2}{c}v_0^2\pi^2n^2\frac{1}{2}\tau,$$

$$= \frac{4}{3}\frac{\pi^2}{c}\frac{v_0^2e^2}{\tau}.$$

The disturbance will be a simple harmonic vibration and correspond to a wave of monochromatic light of wave-length λ.

$$c = \frac{\lambda}{\tau},$$

$$\tau = \frac{\lambda}{c},$$

$$E = \frac{4}{3}\frac{\pi^2e^2v_0^2}{\lambda}.$$

But

$$\tau = \frac{c_1}{v_0^2}; \quad v_0^2 = \frac{c_1}{\tau} = \frac{c_1 c}{\lambda},$$

hence

$$E = \frac{4}{3}\frac{\pi^2 e^2 c_1 c}{\lambda^2} = \frac{C}{\lambda^2}.$$

The energy radiated away from an electron during a collision is inversely proportional to the square of the wave-length of the simple harmonic radiation. This energy radiates away from the electron in form of a simple harmonic wave with the velocity of light.

Let n be the frequency of the light whose wave length is λ, then we have

$$n\lambda = c$$

and

$$E = Cn^2.$$

When the wave travels out into the space the density of the energy in the wave will become smaller and smaller according to the ordinary conception of continuous distribution of the electromagnetic energy. If, however, we assume again, as in the case of Roentgen rays and with exactly the same right, that the energy in the wave front is localized into distinct regions, *i. e.*, along the N Faraday tubes that start from the elementary charge, we find that the average energy of such an electromagnetic unit in the wave of light is equal to

$$E_1 = \frac{C_1 n^2}{N} = kn^2,$$

or the unit of electromagnetic energy in a wave of light is proportional to the square of the frequency.

The theory of thermal radiation as developed by Planck leads to another result. In this theory also the electromagnetic energy appears to be divided up into well separated units; and the unit of energy of radiation is proportional to the frequency of the light.

$$E_2 = hn,$$

$$h = 6.5 \cdot 10^{-27}.$$

In either case these units travel out with invariable properties.

Let us suppose that the units E_1 enter the surface of a metal and are partly converted into kinetic energy of the electron and that the energy of one unit is imparted to one electron. Another part of the energy of the unit may be transformed into other forms of radiations or into heat in the same or opposite way as cathode rays when impinging on different metals produce Roentgen rays of different intensity. We shall suppose that the fraction of the energy of the unit, characteristic for each element, is transformed into kinetic energy of an electron.

$$E = akn^2.$$

The kinetic energy of the electron will be so large that it may overcome the attraction of the positive electricity left behind. The electron may come into collision with molecules before it reaches the surface of the metal and lose a part w of its kinetic energy. Thus the electron leaves the metal with the kinetic energy $akn^2 - w$. When the process is going on the metal will acquire a positive charge and a positive potential P, sufficient to prevent the electrons from escaping. In the case of equilibrium we have

$$Pe = akn^2 - w,$$

e being the change of the electron.

Neglecting w we have

$$Pe = akn^2,$$

$$P = \frac{ak}{e} n^2,$$

$$\tfrac{1}{2}mv^2 = Pe,$$

$$v = \sqrt{\frac{2e}{m} P},$$

$$v = \sqrt{\frac{2ak}{m}} n,$$

v being the initial velocity of the electrons. The velocity of the electrons would be proportional to the frequency of the incident light. Planck's theory, however, would lead to the expression

$$v = \sqrt{\frac{2ah}{m}} \sqrt{n},$$

the velocity would be proportional to the square root of the frequency of the incident light.

The experiments made by E. Ladenburg for a small interval of wave-lengths of ultra-violet light agree quite as well with the first as with the second of these two expressions.

In order to extend the interval of wave-lengths I studied the velocity of electrons emitted from an equimolecular liquid alloy of sodium potassium, that emits electrons even when struck by daylight. The vacuum tubes that were used are shown in Figs. 5 and 6. The tubes are connected with the mercury pump by

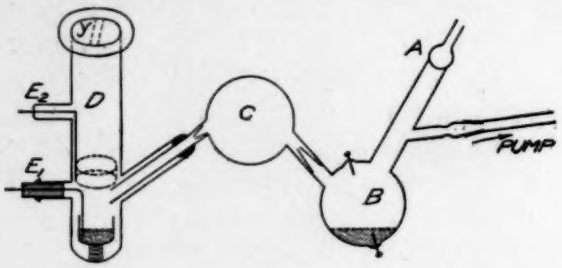


Fig. 5.

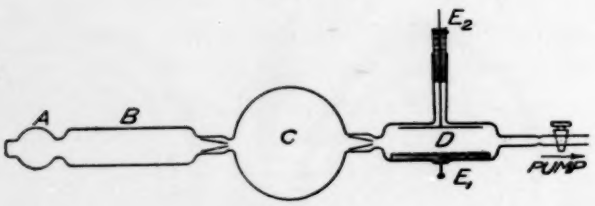


Fig. 6.

means of a ground-joint. When the air has been pumped out the tubes are filled with dry nitrogen, then opened at *A*, where 3 gr. potassium and 1.77 gr. sodium were introduced. The tubes that have been carefully cleaned with a solution of potassium chromate and with distilled water are then sealed off at *A* either by means of sealing wax or by melting the glass directly. The vacuum will be established again and then the metals melted. The surface of the alloy appears to be covered with a dark crust of impurities. The glass walls of the system of tubes are also carefully heated; they give off a considerable amount of gas. The degree of the vacuum

can be estimated by the character of the electrical discharge between the two platinum electrodes in B. It was easy to diminish the pressure so far as to make the discharge very difficult or impossible. The heating of the tubes and the removing of the gas will be repeated several times during two days. The tube of Fig. 5 will then be turned 180° in the ground-joint so that the liquid alloy flows over in the tube C. The tube of Fig. 6 contains a stop-cock so that it could be removed from the pump and the alloy was allowed to flow into the tube C. The crust is held back by means of little funnels of glass between the bulbs B and C. The alloy is almost perfectly clean in the bulb C; the system of tubes is heated again and the rest of the gas developed from the glass walls is removed. In the same way as before, the alloy will be allowed to flow into the tube D, where it arrives perfectly clean. In the tube D of Fig. 5 there is a little glass cup insulated from the outer glass wall by means of amber. The platinum electrode E_1 connecting the alloy with the electrometer, goes through a piece of amber, so that the electrical insulation is as perfect as possible. The electrode E_2 of Fig. 5 consists of a platinum wire connected with a ring of wire gauze touching the glass wall. Two strips of platinum are arranged parallel to one another, leaving free a slit similar to the slit L through which the beam of light passes. The tube of Fig. 6 is held in its final position by means of well insulating paraffine. The electrode E_1 is directly connected with the alloy through the glass, while the negative electrode E_2 is insulated by a piece of amber. The electrode E_2 is a slip of platinum foil about 1 cm. wide and 4 cm. long. By turning the tube round its axis the distance between the two electrodes E_1 and E_2 could be chosen at liberty. It was usually about 0.5 cm. Thus prepared the tubes were sealed off from the pump.

The general arrangement of the experiment is shown by Fig. 7. A parallel beam of light produced by an arc and a condenser, passed through a small slit L_1. A system of lenses produced a sharp image of this slit on the screen L_2 which was endowed with a millimeter scale. The beam was then deflected by means of a total reflecting prism and decomposed in the spectrum by an ordinary prism. The tube of Fig. 6 was mounted in a wooden box,

one side of which possessed a metallic window that could be moved up and down so that the light struck the metal to be tested. The whole box could be displaced also along the scale L_2. The electrode E_1 was connected to a commutator through a long wire insulated by pure paraffine. The commutator was made of paraffine and little glass cups. One pair of the quadrants of the electrometer was charged with the positive electricity of the alloy, whereas the other pair through the commutator was connected to

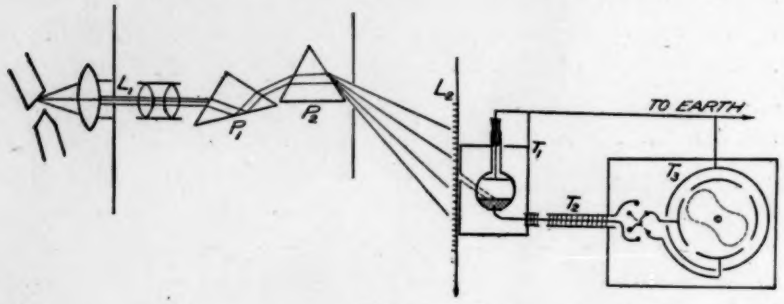


Fig. 7.

the electrode E_2 and to earth. The wooden box T_1 containing the glass tube, the tube T_2 and the box of the electrometer were covered with tin foil connected to earth. The quadrant electrometer had a fine quartz suspension and amber insulation. The needle was charged from a storage battery to a potential of about 12 volts. In spite of the care that was taken in insulating the system, there was always a small leakage, the amount of which could easily be taken account of. The electrometer was calibrated by means of accumulators and resistances. The electromotive force of the storage battery was determined with a potentiometer.

If the system of tubes of Fig. 5 was used the two prisms P_1 and P_2 were turned so that the beams of the spectrum fell in a nearly perpendicular direction upon the alloy. As in this case the distance between the metal and the negative electrode E_2 was about 2 cm.; the potential measured appeared to be smaller than that measured with the other tube. Moreover, the surface of the alloy in the tube of Fig. 5 oxidized in about four or five days after its preparation, so that for further measurements the alloy had to be replaced,

whereas the vacuum in the tube of Fig. 6 remained constant and the surface of the alloy perfectly clean for an apparently unlimited time. Nor could I in the last case discover any trace of photoelectric fatigue.

The first question to answer was the influence of the intensity of the light. I found that the potential difference between the two electrodes E_1 and E_2 was constant and independent of the intensity of the light. If the alloy was struck by a very strong beam of white light from the arc, or by daylight, or by the weak light that remained after the strong beam from the arc had passed through a sheet of snow and water of about 1 cm. thickness placed between the arc and the alloy, the deflection of the electrometer was always the same corresponding to a potential difference of 1.12 volts. In addition the potential difference thus determined was that due to the action of the shortest violet rays in the spectrum. It should be mentioned, however, that the deflection became decidedly smaller when the intensity of the light fell below a certain value. When, for instance, I darkened the room of the experiment, or when the beam from the arc was forced to go through a glass plate blackened with lamp black, the deflection of the electrometer became considerably smaller. This is probably due to the fact that the number of electrons emitted per unit time depends on the intensity of the light. If now the number developed per unit time becomes very small, saturation of the metal and of the electrometer becomes impossible and the deflection of the electrometer drops down. There is another phenomenon whose nature is not yet plain, in which the intensity of the light plays a part, namely, the red end of the spectrum beyond the yellow region where the photoelectric effect begins, produces also a small and irregular effect, depending on the intensity of the light and on the heat of the rays in this part of the spectrum.

J. A. Fleming[1] measured the photoelectric effect by means of a galvanometer and found that the galvanometer deflections increase very rapidly with the intensity of the incident light. This observation is not in contradiction to the constant deflection of the electrometer over a large range of intensities, because the galvanometer

[1] J. A. Fleming, "A Note on the Photoelectric Properties of Potassium Sodium Alloy," Phil. Mag., 6th s., Vol. 17, p. 286, 1909.

deflexions depend not only upon the velocity of the electrons but also upon the number emitted per unit time.

On reversing the potentials on the quadrants of the electrometer by means of the commutator I was able to take the readings to the right and left, and I took as a rule four readings on either side. The mean values λ of eight readings for each position of the tube in the spectrum are given in the following table as a function of the wave-length λ of the incident light.

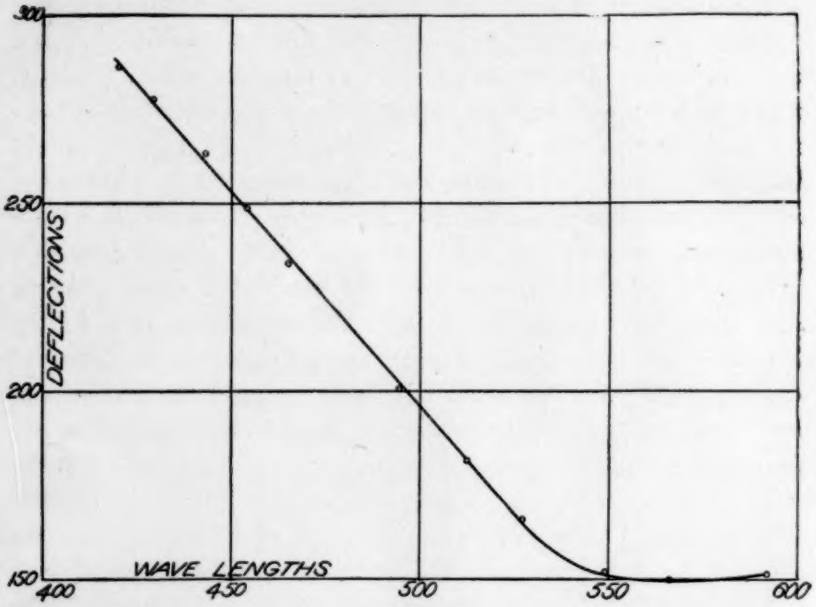


Fig. 8.

λ	λ Observed.	λ Calculated.
592	151.8	—
566	149.9	—
549	152.1	—
527	166.0	166.0
712.5	181.5	180.7
494.5	200.9	201.4
465.0	234.03	236.1
454	248.4	249.0
443	263.2	261.1
429	279.0	278.0
420	286.5	288.3

The numbers are represented in Fig. 8. The experiment has

often been repeated with the same result. The spectrum was calibrated by means of the following lines:

Li	670.8	Ag	546.6
Li	610.4	Ag	521
Na	589.0	Li	497.2
Hg	577	Li	460.2
Hg	546	Hg	436

The potential difference between the electrodes of the vacuum tube appears to be proportional to the wave-length and decreases with increasing wave-length. The figures calculated on this assumption are given in the table. The difference between the deflections calculated and observed exceeds in no case 2 per cent.. This law seems to hold good only to wave-lengths of about 520 $\mu\mu$. From this point up to the wave-length of 582 $\mu\mu$ the connection between the potential of the alloy and the wave-length is almost a straight line. Beyond this point the deflections become small very rapidly and irregular at the same time. These irregular deflections depend partly on a heat effect, when a layer of water is introduced in the path of the light, the deflections decrease but they do not quite disappear. So far as these preliminary experiments go they seem to indicate that the velocity of the electrons is independent of the intensity of the light and that the kinetic energy is proportional to the frequency of the incident light.

$$Pe = ah\nu,$$

$$n\lambda = 3.10^{10},$$

the maximum deflection was found for a wave-length of 420 $\mu\mu$, corresponding to a potential difference $P = 1.12$ volts.

$$\lambda = 4.2 \cdot 10^{-5} \text{ cm.},$$

$$n = 0.715 \cdot 10^{15},$$

$$e = 1.55 \cdot 10^{-20} \text{ absolute electromagnetic units},$$

$$P = 1.12 \cdot 10^{8} \text{ absolute electromagnetic units},$$

$$Pe = 1.74 \cdot 10^{-12},$$

thus

$$ah = 2.425 \cdot 10^{-27},$$

$$h = 6.5 \cdot 10^{-27},$$

$$a = 0.37.$$

The velocity of the electrons emitted under the action of violet light of wave-length 420 is given by the equation

$$\tfrac{1}{2} mv^2 = Pe\,,$$

$$v = \sqrt{2\frac{e}{m}P},$$

$$\frac{e}{m} = 1.77 \cdot 10^7\,,$$

$$v = 6.3 \cdot 10^7 \text{ cm./sec.}$$

Many problems spring up in connection with the present investigation, which was carried out in the physical laboratory of the University of Michigan. I shall extend the research in different directions. A small addition to this paper has already been published in the August number of this journal.

COUNTER ELECTROMOTIVE FORCE IN THE ELECTRIC ARC.

By C. D. Child.

IN a somewhat recent article by Becknell[1] it was shown that there was an E.M.F. of approximately .7 volt between the terminals of an arc after the impressed E.M.F. was removed. This may be explained as being due to the difference of temperature between the two carbons, and a few simple tests of such an explanation have been tried by the present writer and are described in the following article.

This subject has been so intimately connected with the discussion of the existence of a counter E.M.F. in the arc, that some remarks on this latter subject may not be out of place. It may seem like bringing back to life what has been decently buried to discuss this again, but the subject has one phase which I believe has never been properly considered, namely, the exact meaning which different writers give to the expression "counter E.M.F." when applied to the arc.

Meaning of Expression "Counter E.M.F." — It would appear as if this term should mean the same when applied to the arc as when applied to a motor, or a storage cell. In those cases we find: first, that the potential difference between the terminals of a cell or motor does not obey Ohm's law; secondly, that there is an E.M.F. remaining after the impressed E.M.F. has been removed and that this is of sufficient magnitude to account for the deviation from Ohm's law; and thirdly, that in the majority of cases the electrical energy is changed into something besides heat energy.

In the arc only the first of these properties is found to exist. In fact the arc deviates from Ohm's law much as other forms of discharge through gases deviate, where the expression counter E.M.F. has never, I believe, been applied.

[1] Phys. Rev., 21, 181, 1905.

In the beginning of the investigation on the arc it was not known that this was the only point of similarity between the arc and a cell, and writers using the word no doubt had in mind a counter E.M.F. identical with that of the cell. Later writers have used the term merely to mean that the potential difference of the arc deviates from Ohm's law in a definite manner, and have so defined it. Yet no one seems to have pointed out that the meaning of the word as defined by Duddell, for example, is not the same as the meaning which Edlund had in mind, nor the meaning generally given to the term in physics. This has led to more or less confusion in what has been written on the subject during the past few years. For example, one occasionally sees the statement that it has at last been definitely shown that there is a counter E.M.F. in the arc. The fact is that on the one hand it has neither recently nor at any other time been shown that the arc has more than the first of the three peculiarities mentioned above, and on the other it has never been doubted but that there was this one point of similarity between the arc and the cell.

Because of this confusion in the use of the term it seemed to the present writer that a brief account of the different types of experiments on this subject and of the different meanings of the words used which have accompanied these experiments will be of some value.

The discussion had its origin in an attempt by Edlund[1] to explain the relation between the "apparent resistance" of the arc and its length. By "apparent resistance" he meant the ratio between the potential difference at the terminals of the arc and the current. This ratio he found equal to $a + bl$, where l is the length of the arc and a and b are constants depending on the kind of carbons used. The first term of this expression he considered to be due to a counter E.M.F. equivalent to 23 Bunsen cells.

Others questioned the existence of such an E.M.F. and several different methods have been used to test the question. These methods may be divided into two general classes: First, methods which attempt to find a counter E.M.F. by measuring the resistance of the arc, and second, those attempting to find it by measuring the E.M.F.

[1] Pogg. Ann., 131, 595, 1867; 133, 353, and 134, 250, 1868.

remaining between the carbons after the impressed E.M.F. has been removed, or what we may call the residual E.M.F. of the arc.

Those who attacked the problem by measuring the resistance of the arc have assumed that the counter E.M.F. was the difference between the potential difference at the terminals of the arc and that part of it which appeared to obey Ohm's law. In other words that $E' = E - RI$, where E' is the counter E.M.F., E the potential difference at the terminals, R the resistance of the arc, and I the current.

Meaning of "Resistance of the Arc." — We find, however, that "resistance of the arc" has meant four different things with different experimenters, and with these different meanings there are corresponding differences in what is meant by counter E.M.F.

First of all it has been used to mean the ratio between the potential difference at the terminals and the current. This, however, has usually been called the "apparent resistance."

Secondly, it has been used to mean the term bl in the expression $r = a + bl$, which was used by Edlund, namely, the part of the apparent resistance which was proportional to the length of the arc. This Edlund called the "true resistance."

At a later time it was used to mean the ratio between a small increase in E and the corresponding increase in I, or what we may call dE/dI. An approximation to this was made by those who used some modification of the Wheatstone bridge.

Finally it was pointed out by Luggin[1] that any change in the current through the arc produced a corresponding change in both the vapor of the arc and the shape of the carbon; so that one does not have the same arc after the current has been increased as before The methods which are modifications of the Wheatstone bridge do not correctly measure either the resistance of the arc in its first condition, nor its resistance after the current has been increased. This difficulty has been clearly stated by Mrs. Ayrton,[2] Duddell[3] and others. They have, therefore, defined the true resistance of the arc as the ratio between a small change in potential difference and the corresponding change in the current, when the change is made so

[1] Centralbl. f. E. T., 10, 591, 1888.
[2] The Electric Arc, p. 400.
[3] Phil. Trans., 203, A, 306, 1904.

small, or for so short a time, that the condition of the arc itself does not vary. In other words the resistance as thus defined is the partial derivative of the potential difference with respect to the current which we shall indicate by $\partial E/\partial I$.

This would undoubtedly be the correct way of defining the resistance, if it were not for the doubt which must exist in one's mind as to whether it is possible to have a change in current without having a change in the condition of the arc. If the current in the arc is carried by ions, as we have reason to believe it is, it is not possible to change the current without changing either the number of the ions or their velocity. In either case there would be a change in the condition of the gas. However, this definition may properly be considered as giving a limiting condition toward which a close approximation may be made.

Resumé of Experiments on Resistance and Counter E.M.F. — Since Edlund's time there have been many experimenters who have examined the relation between the potential difference at the terminals of the arc and the length and current, and as far as their experiments were correct they gave results similar to those of Edlund.[1]

As has been shown by different experimenters, these results prove nothing definite concerning the existence of a counter E.M.F., and we need not consider them further in this connection.

If we pass to other methods of attacking the problem we find that Swendler[2] gave the value of the counter E.M.F. as 2 volts, but since he did not divulge his method of arriving at this conclusion we are unable to judge of the importance of his work.

As far as we know the first experimenter to use a method different from that of Edlund's was von Lang,[3] who endeavored to measure the resistance of the arc by a modification of the Wheatstone bridge. He found the resistance to be 1.82 ohms and concluded that the counter E.M.F. was 38.9 volts. This method gave approximately the value of the resistance as defined the third way, namely, dE/dI.

[1] Ayrton and Perry, Proc. Phys. Soc., 5, 197, 1882. Frohlich, Elektrot., Z. S., 4, 150, 1883. Peukert, Elektrot., Z. S., 7, 443, 1885. Nebel, Centralbl. f. E. T., 8, 517 and 619, 1886. Cross and Shepard, Proc. Amer. Acad. Science, 86, 2, 1886. Uppenborn, Centralbl. f. E. T., 9, 663, 1887. Luggin, Centralbl. f. E. T., 10, 567, 1888.

[2] Lond. Elec., 2, 107 and 117, 1879.

[3] Centralbl. f. E. T., 7, 443, and Wied. Ann., 6, 145, 1885.

Attempts were then made to find the resistance when the change in the current was made much smaller, that is, to get the value indicated by the expression $\partial E/\partial I$. Arons[1] attempted to do this by using a different modification of the Wheatstone bridge. The arc with the battery producing it was used as one branch of the Wheatstone bridge. Instead of the battery ordinarily used with the bridge a transformer was used and instead of a galvanometer a dynamometer. The three arms of the bridge were adjusted until no current was shown by the dynamometer. The resistance of the arc could then be determined. The resistance was found to be approximately 2 ohms and the counter E.M.F. 40 volts. Luggin[2] used a different modification of the bridge and Firth[3] still another, both getting results similar to those of Arons.

Negative Resistance. — In 1895 Ayrton[4] concluded from the result of a few simple experiments that the resistance of the arc was negative. What he measured was dE/dI. It had been previously pointed out by Luggin that this quantity was negative, and it has since been shown even more clearly by the curves given by Mrs. Ayrton.[5] If one is to define resistance, as meaning dE/dI, there is no question but that the resistance of the arc is a negative quantity, but of all the uses of the word this is perhaps the least justifiable, and to speak of a negative resistance is, to say the least, misleading.

The word resistance means primarily something which hinders the movement of some object. An electrical resistance means something which hinders the flow of an electric current, and the most natural meaning of the expression "negative resistance" would be something which helps the flow of the current. It is needless to say that the resistance of the arc does not help the flow of current.

Firth and Rogers[6] superimposed an alternating current on the direct current through the arc, and the resistance of the arc to this alternating current was taken as its resistance. Frequencies between

[1] Wied. Ann., 30, 93, 1887.
[2] Centralbl. f. E. T., 10, 43, 1888.
[3] Mem. and Proc. Manchester Lit. and Phil. Soc. (4), 9, 139, 1895.
[4] The Electric Arc, p. 75.
[5] The Electric Arc, p. 113.
[6] Phil. Mag. (5), 42, 407, 1896.

7 and 250 complete alterations per second gave the same resistance. They, therefore, believed that the changes in the current were so rapid that there were no corresponding changes in the arc. The value of the resistance which they found varied much with different carbons and with different currents. Values ranging from 2 to — 2 ohms are given by them. The corresponding values of the counter E.M.F. were in the neighborhood of 40 volts.

Following the investigation of Firth and Rogers was a careful examination of the counter E.M.F. and resistance by Duddell.[1] His principal advance over the work of others consisted first in devising a method by which one could test whether the arc remained constant during the change in current or not, and secondly, in using much higher frequencies than those which had previously been used.

To decide whether the arc changed any or not he imposed a small alternating current on the direct current which was passing through the arc, and determined whether this alternating current was in phase with its E.M.F. or not. Ordinarily, when an alternating current is thus used, it lags behind its E.M.F. Duddell assumed that if the two were in phase the condition of the arc had not changed during the change in current. He found that for low frequencies with solid carbons the oscillations were 180° out of phase, and that to have the two in phase with such carbons it was necessary to have frequencies of 100,000 or more per second. For cored carbons 26,000 alternations per second were needed.

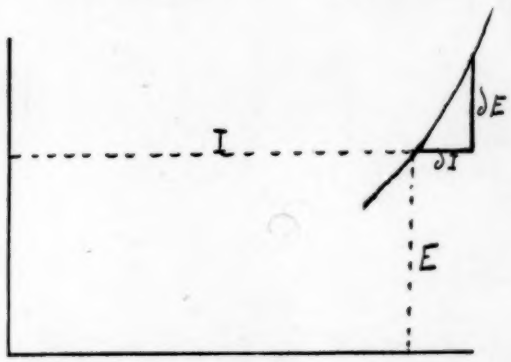
When the alternating current was in phase with its E.M.F. the ratio between the E.M.F. and the current was taken as the "true resistance" of the arc, and the counter E.M.F. was found from the formula $E' = E - RI$. The value of E' as found by him varied from 11.2 to 18.5 volts with different currents and different carbons.

"*Forward E.M.F.*" — He also endeavored to find the part of the arc where this counter E.M.F. was situated. For this purpose he inserted an exploring pencil in the arc and found the potential difference between this and the anode, both for the direct and for the superimposed alternating current. From this data he computed the counter E.M.F. near the anode, using the same method as that given above. This he found to be approximately 17 volts. A similar set of

[1] Phil. Trans., 203, A, 305, 1904.

readings gave a "forward E.M.F." near the cathode of 6 volts, the two accounting for the 11 volts which was found in this particular case for the whole arc.

This again is a use of words which in one sense is entirely correct, and yet is entirely misleading. Duddell undoubtedly found the value of $E - RI$ near the cathode to be a negative quantity, and since he had called this a counter E.M.F. when it was positive, it is not surprising that it should be called a "forward E.M.F." when it was negative. Yet to do so gives one the impression that there is an E.M.F. at the cathode of the order of six volts, which changes some other form of energy into electrical energy. In reality there is no reason whatever to suppose that there is any such E.M.F. at that point. All that Duddell's experiment showed was that $\partial E/\partial I$ was greater than E/I between the gas of the arc and the cathode. In other words, that the form of the curve showing the relation between the cathode drop and the current was that shown in Fig. 1.



F.g. 1.

This is the same kind of curve that one finds when examining the relation between the potential difference and the current for discharge produced by Röntgen rays. No one ever speaks of a "forward E.M.F." with such discharge and there would appear to be no more reason for using that expression in connection with the arc.

Reinke[1] compared the counter E.M.F. from observations made on the whistling arc. His method was in principle the same as that

[1] Verh. d. V. z. Beford. d. Gewerbfliesses, 83, 403, 1904.

of Duddell's, but the alternating current was produced by the arc itself, and not by a separate dynamo. The current in a whistling arc is equivalent to a small alternating current superimposed on a direct current. He says concerning it that "only about one eighth of the observed potential difference, namely, in this case about 6 volts, was used in overcoming the ohmic resistance of the arc, while the remainder, namely, about 40 volts, is to be considered a polarized potential difference, or counter E.M.F. (cathode and anode drop in potential)."

We may sum up these results by saying that they show that the potential difference between the terminals of the arc varies when the current is varied in much the same way as the potential difference between the terminals of the cell of a storage battery, but they show nothing, of course, concerning the phenomena occurring after the impressed E.M.F. is removed. For this purpose we must examine the second group of experiments.

Residual E.M.F.—The second method of testing for a counter E.M.F. in the arc was to measure the residual E.M.F. after the impressed E.M.F. was removed. There is no question of the meaning of terms involved in these measurements and there is apparently no great experimental difficulty, and yet there has perhaps been as great disagreement among experimenters concerning such an E.M.F. as concerning any question in physics.

Edlund[1] not only suggested a counter E.M.F. as explaining the relation which he found between the potential difference at the terminals of the arc and its length, but endeavored to find a corresponding residual E.M.F. He passed a current from a number of cells through the vapor of the arc after the impressed E.M.F. had been removed, passing it first in the direction of the supposed E.M.F. and then in the opposite direction. He found the current in the first direction to be the greater. To compare the E.M.F.'s in the two cases he eliminated the resistance of the circuit by using Ohm's law, but Ohm's law does not at all apply to the case of discharge through hot vapors, and the supposition in this case introduced a very large error. He was led to believe that the counter E.M.F. was equivalent to 10 or 15 Bunsen cells.

[1] Pogg. Ann., 134, 250 and 337, 1868.

But eight years before this Wild[1] had measured this same quantity by throwing the arc with a double-throw switch from the batteries to a high resistance galvanometer. He was not able to determine the E.M.F. accurately, because the resistance of the vapor between the carbons was not known to him, but he concluded that it was more than 100 times as great as the E.M.F. produced by a copper-German silver couple having the same difference of temperature at its terminals. This statement, indefinite though it is, is more accurate than any statement of residual E.M.F. made for several decades thereafter.

After Edlund's experiments there were a series of observations by different experimenters, giving all kinds of values from zero to two volts. The fact that many of the earlier experimenters found no residual E.M.F. is less surprising, since they were looking for one comparable with the supposed counter E.M.F. of the arc, and we can now say definitely that there is none of this order of magnitude. But that some of the later experimenters should have differed so decidedly as to a small residual E.M.F. is hard to understand.

Lecher,[2] Luggin,[3] Corbino and Liga[4] concluded that there was no residual E.M.F. Strenger[5] concluded that if there was one it was small compared with 10 volts. Hertzfeld[6] thought at first that he had found one, but afterwards concluded that the observed effects were due to thermo-junctions outside the arc. Le Roux[7] found a residual E.M.F. but did not give its magnitude.

Arons[8] thought that the vapor remaining between the carbons after the impressed E.M.F. was removed was not conducting for small voltages, and that it was necessary to apply 18 volts in order to get any current through it.

Granqvist[9] showed that Arons's failure to get a current with lower voltages was due to using a non-sensitive galvanometer. Granqvist

[1] Pogg. Ann., 111, 624, 1860.
[2] Wien. Sitzungsberichte, 95, 11, 992, 1887.
[3] Wien. Sitzungsberichte, 98, 1 and 192, 1889.
[4] Monash, Der Elektrische Lichtbogen, p. 134.
[5] Wied. Ann., 45, 33, 1897.
[6] Wied. Ann., 62, 435, 1897.
[7] Lum. Elec., 3, 285, and C. R., 92, 709, 1881.
[8] Wied. Ann., 57, 185, 1896.
[9] Beib., 22, 243, 1898.

himself was able to pass a current from one Daniell cell. His method was similar to Edlund's, except that he used a rotating switch which closed the galvanometer circuit .0009 second after the main circuit was broken. He also assumed Ohm's law to hold, but his voltages were much smaller than those of Edlund's, so that the error which was introduced in his calculations was much smaller. He found a residual E.M.F. of .23 volt in the opposite direction to that of the impressed E.M.F.

Blondel[1] using a method almost identical with that of Granqvist concluded that there was no E.M.F. 1/600 second after the arc was interrupted as great as .16 volt. He used both solid and cored carbons, long and short arcs, changed the time between the disconnection of the arc from the main circuit and the connection to the galvanometer circuit, and in other ways varied the conditions as far as possible.

On the other hand Hotchkiss,[2] using an oscillograph having a period of .0002 second, found indications of an E.M.F. This was less than than .66 volt, but was still clearly discernible. Milkiewicz[3] found a residual E.M.F. of from 1.5 to 2 volts. And Becknell[4] found an appreciable E.M.F. existing for several seconds after the impressed E.M.F. was removed. He determined the amount by balancing it against a known potential difference by means of a sensitive galvanometer. The maximum was .63 volt, which occurred .3 second after the removal of the impressed E.M.F. When the arc was first extinguished the resistance was small, but increased very rapidly with the time. He showed that the residual E.M.F. was not due to the thermal junctions outside the arc.

It is very difficult to reconcile the work of Blondel with that of the others. Furthermore, it is hard to see how it could be otherwise than that there is such a residual E.M.F. It was shown by Dubs[5] and Olivette[6] that the current flows from a cooler carbon to one very hot. This may amount to several volts. All the phe-

[1] Lond. Elec., 39, 615, 1897.
[2] Trans. Amer. Phys. Soc., 2, 1901.
[3] Science Abs., 7, 360, and Beib., 27, 465, 1903.
[4] Phys. Rev., 21, 181, 1905.
[5] Centralbl. f. E. T., 10, 749, 1888.
[6] Lond. Elec. Rev., 31, 728, 1892.

nemena observed by Becknell are such as would be expected from the difference in temperature of the carbons. There is probably a very small area on the cathode which is as hot as the anode, so that when the impressed E.M.F. is first removed the difference in temperature between the electrodes is small. The area of this high temperature on the cathode is small. It will, therefore, cool more quickly than the anode, so that the difference in temperature between the electrodes at first increases. This would correspond to the increase in the residual E.M.F. observed by Becknell. The observed residual E.M.F. is in the right direction, since the anode is hotter than the cathode after the arc is extinguished.

Test of Explanation. — This explanation can be tested by changing in some way the temperature of the electrodes. The greatest change in the residual E.M.F. may be expected when the anode is

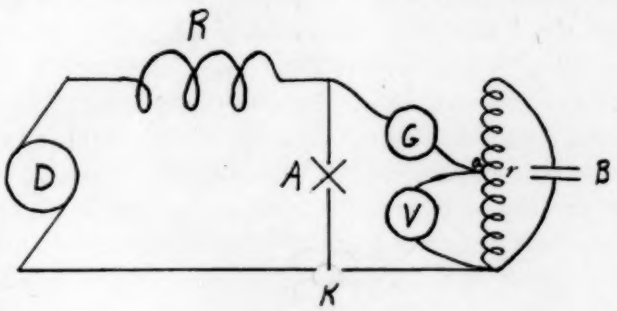


Fig. 2.

cooled, for under ordinary conditions it is hotter than the cathode, and when cooled we should expect the E.M.F. to be diminished or reversed.

In the first experiments performed by the writer to test this explanation a hollow carbon was used for the anode and water was caused to flow through this. The method of determining the E.M.F. was the same as that used by Becknell. The connections are shown in Fig. 2. *A* is the arc, the current coming from the dynamo *D* through a regulating resistance *R*. *K* is the key for switching the arc from the dynamo circuit to the testing circuit. This circuit consists of the galvanometer *G* and the variable potential difference which is balanced against the E.M.F of the arc. The

galvanometer used gave a deflection of 1 mm. with the scale 60 cm. from the mirror, when there was a potential difference of 3.5×10^{-5} volt. The potential difference in r was maintained by two cells at B, and could be varied by changing the point a on the resistance r. It was measured by a Weston voltmeter at V. A pendulum was used to change the connections at K. This had no advantge over the rotating wheel used by Becknell, except that there happened to be a pendulum arranged for this purpose in the laboratory. The time between opening the dynamo circuit and closing that to the galvanometer could be varied from .03 to .5 second.

It was found very difficult to balance the residual E.M.F. against a potential difference in r, because the E.M.F. never appeared to be twice the same. Becknell found it necessary to run the arc a minute before making observations and also to have it so that it did not run over the crater, but in the experiment here described it was not practical to fulfill either of these conditions. The arc could not be allowed to run for a minute, for if it was, the carbon was apt to be burnt away, so as to allow the water to leak through and put out the arc. And this difficulty could not be remedied by having thicker walls for the carbon tube, for with thick walls no effect at all could be detected when the water was sent through it.

Neither could the crater be properly formed, for the carbon was liable to be burnt through before this could be done. Moreover, with a cooled anode the arc is much more variable than with a hot anode. As a result no attempt was made to take a series of observations, but only to show definitely that the residual E.M.F. was reduced by cooling the anode.

The apparatus was first tested with ordinary cored carbons with results very similar to those of Becknell's. Then the cooled carbon was substituted for the hot anode. The outer diameter of this before the arc had burnt any of the carbon away was 12 mm. and the inner diameter was 4.4 mm. This was cooled by allowing water from the tap to run through it. The current was approximately 10 amperes and the length of the arc 2 mm. With the cooled carbon the E.M.F. was approximately .27 volt .03 second after the impressed E.M.F. was removed, decreasing gradually to .22 volt .17 second after the removal of the E.M.F. The corresponding num-

bers given by Becknell are .37 volt and .52 volt respectively.[1] After .17 second the space between the electrodes had lost its conductivity to so great extent that further measurements were difficult.

The cathode was then cooled, but no change could be definitely shown. Since the hot point on the cathode is smaller than that on the anode and consequently must be expected to cool more rapidly than the anode, it would not be expected that cooling the cathode artificially would produce as large an effect as cooling the anode.

It was desired to show the change more strikingly, if possible, and for this purpose a hollow brass tube was used for the anode and this was kept cool as before by causing water to flow through it. A new difficulty was here met. The region between the electrodes was found to be nearly non-conducting after the arc was extinguished. It was only by having the electrodes very near together and by making the observation as soon after the impressed E.M.F. was removed as possible, that sufficient current could be passed between the electrodes to affect the galvanometer. Even then there was not always a movement of the galvanometer needle, but whenever there was, the deflection was such as to indicate a residual E.M.F. in the opposite direction to what it is normally. The time between opening the dynamo circuit and closing the galvanometer circuit was .03 second. The length of the arc was approximately 1 mm.

When the cooled brass tube was used for the cathode it quickly became coated with a layer of carbon and did not then behave differently from what it would if it had been a cooled carbon tube.

Residual E.M.F. in a Vacuum. — The arc was then tried in a vacuum of approximately .02 mm. of mercury pressure. Under these conditions the anode is not heated as quickly as in the air, nor does it appear to reach as high a temperature as in the air. The residual E.M.F. in this case is somewhat smaller than in air, but it depended so much on the length of time that the arc had been running and on the way that it happened to jump from one point to another that no measurements were made when both electrodes were carbon.

It was found that conditions could be much improved by using mercury instead of carbon for the anode. This, of course, never

reaches a high temperature, and this arrangement showed most successfully of all the effects produced by having the anode at a comparatively low temperature. With this there was a residual E.M.F. of nearly one volt in the opposite direction to the ordinary residual E.M.F. The exact value depended very largely on where the cathode end of the arc happened to be at the time the switch K was changed; .03 second after the impressed E.M.F. was removed the residual E.M.F. was .8 volt or more, if the cathode had been at the bottom of the carbon, and somewhat less than this if it had been at the side.

As near as could be determined the residual E.M.F. did not decrease appreciably during the brief time that the region between the electrodes remained conducting. No current could be passed of sufficient amount to affect the galvanometer used, .14 second after the impressed E.M.F. was removed.

Although it is well known that a hot carbon in a vacuum gives off negative ions and charges bodies in its neighborhood negatively, it seemed well to test this explanation further by substituting a carbon pencil that could be heated by an electric current for the cathode of the arc in the preceding experiment. This was done and it was found that there was an E.M.F. between the hot carbon and the mercury in the same direction as before.

SUMMARY.

A review of the literature on the subject of the counter E.M.F. of the electric arc shows that this expression has been used with several different meanings and the most recent meaning is not the same as that given to the expression when applied to a cell or an electric motor.

A review of the literature on the residual E.M.F. of the arc shows that the majority of experimenters have found such an E.M.F. whose value was somewhat less than one volt. This E.M.F. has been explained as being due to the difference in temperature of the electrodes. This was tested by cooling the anode by three different methods and the results were in harmony with such an explanation.

COLGATE UNIVERSITY,
July, 1909.

ON THE ELECTRICAL CHARACTER OF THE SOURCE OF LIGHT RADIATION.

By T. P. Irving.

THE experimental and theoretical studies of Lenard, J. Stark, Fredenhagen and others, concerning the source of light radiation, have led them to conclusions that differ rather widely.

Lenard[1] drew the following conclusions from his examination of the spectra and electrical wandering of substances volatilized by the electric arc and by the Bunsen flame in an electrical field: (1) "The emission centers of the principle series are electrically neutral metal atoms." (2) "The emission centers of the subordinate series are positively charged metal atoms, that is, such as have lost elementary quantities of negative electricity."

Fredenhagen[2] from his study of substances volatilized in oxygen and non-oxygen flames, in the divided Bunsen flame, and in the vacuum lamp arrived at conclusions that may be summed up as follows: (1) The principal series comes from an oxygen compound of the metal, and are due to the processes of combination between the metal and oxygen. (2) The subordinate series come from the metal itself, and are due to the process of change which a metal atom undergoes while acquiring or losing one, two or more negative electrons.

J. Stark[3] from his study of the Doppler effect in canal rays comes to the following conclusions: (1) "The carriers of the line series are positive ions." (2) "The centers of emission of the line spectrum are negative electrons." (3) "The carrier of the band-spectrum is a neutral atom constituting a system made up of a positive atom (Restatom) and a negative electron."

[1] Drude Ann., IX., p. 642, 1902; XI., p. 636, 1903; XVII., p. 197, 1905.

[2] Drude Ann., XX., p. 133, 1906. Phys. Zeit., VIII., pp. 404, 729, 1907.

[3] Drude Ann., V., p. 421, 1901; VIII., p. 257, 1902; IX., p. 666, 1902; XIII., p. 669, 1904. Wien and Planck Ann., XXI., p. 401, 1906. Phys. Zeit., VII., p. 355, 1906. Die Elektricität in Gasen, Leipzig, 1902.

J. J. Thomson[1] from his experiments concludes: "The 'candle spectrum' is the spectrum of carbon when the atom is charged with negative electricity, or of some compound of carbon in which its atom is negatively charged." Further he finds the red and green hydrogen lines from both negative and positive hydrogen. W. J. Humphreys[2] thinks that possibly "the only origin of spectrum lines is the shock of 'restatoms' by swiftly moving negative corpuscles." Pringsheim[3] and Smithells[4] look upon chemical processes as simultaneous with the production of light radiation, and Pringsheim favors the view that the coloration of a flame is due to a reduction process. Hartley[5] holds that only the *D*-lines are present when metallic Na is volatilized in a flame, whereas the spectrum derived from some salt of Na gives not only principal lines, but also the subordinate series of lines. A. S. King,[6] C. de Watteville[7] and Paschen[8] think that light-emission is largely a thermal effect. R. W. Wood[9] has obtained a resonance spectrum from Na vapor by a method which precludes chemical action.

Thus it appears that some ascribe the light-radiation to matter in an electrically positive, negative or neutral condition; others ascribe it to chemical processes; and others to thermal, resonance, or other phenomena.

It might be suggested that the electrical condition and the chemical and other processes are but diverse causes of one and the same final state of a substance, and that such final state is necessary to the production of the radiation. In one case this state may be brought about by oxidation or reduction, in a second by light excitation, in a third by electrical condition, and so on. If the radiation arises from such a final state due to different causes acting singly or in combination, the interpretations given by the different investigators to their results are probably right so far as attempted, but

[1] Proc. Roy. Soc., LVIII., p. 244, 1895.
[2] Astrophys. Jour., XXVII., p. 200, 1908.
[3] Weid. Ann., XLV., p. 459, 1892.
[4] Phil. Mag., 5, XXXIX., p. 133, 1895.
[5] Proc. Roy. Soc., A, LXXIX., p. 242, 1907.
[6] Astrophys. Jour., XXVII., p. 353, 1908.
[7] Phil. Trans., A, CCIV., p. 139, 1905.
[8] Weid. Ann., L., p. 409, 1893; LI., pp. 1, 40, 1894; LII., p. 209, 1894.
[9] Phil. Mag., 6, XV., p. 581, 1908.

are incomplete. A theory, broader than the present rather special and conflicting theories, is needed to harmonize the interpretations of experimental evidence. The formulation of such a theory requires further knowledge. The various conditions under which the radiation is obtained must be examined and compared; its supposed different causes must be studied more thoroughly not only in themselves, but also in relation to one another.

The author of this paper has attempted to acquire some of the needed knowledge, through studying simultaneously the electrical and spectroscopic characters of the divided Bunsen flame, both in its simple state, and when colored by metals or salts.

(*A*) Description of Apparatus and Method of Investigation.

The burner used to separate the cones of the Bunsen flame consisted of an inner brass tube (*a*) 22 cm. long and 1.4 cm. in diameter and an outer glass tube (*b*) 15 cm. long, 5.1 cm. in diameter at the bottom and 3 cm. at the top, fitted over the brass tube by means of a bored plug. This form of glass tube was used by Fredenhagen. It is much more satisfactory than the straight tube, since it gives an outer cone so steady and regular that any bending of this cone, due to an electrical field, can be detected with certainty. So far as could be ascertained no vapors were introduced into the cones by the substances of the tubes. The device for mixing the gas, air and vapor consisted of a glass bulb (*c*) 6.7 cm. in diameter, fitted over the bottom of the tube (*a*) and connected at its side with the neck of the retort (*d*) which contained the solution. The gas entered at the bottom of the bulb through the tube (*e*), 1.5 cm. in diameter, drawn out so as to leave an opening .08 cm. in diameter for the issuing of the gas, and extending up into the brass tube a few mm. By this arrangement of burner and mixing device the cones could be kept burning steadily for a long time.

The method used for introducing the vapor into the burner is that described by Beckmann.[1] An acid solution of a salt and a few small pieces of coppered zinc are placed in the retort (*d*). The metallic vapor given off together with the proper quantity of air

[1] Zeitsch. für Angewandte Chemie, p. 561, 1907.

admitted through the loosely stoppered tubular of the retort, pass into the bulb (*c*) and mix in the tube (*a*) with the gas issuing from (*e*). The gas used was the illuminating gas from the mains of the city of Washington.

When the supply of air and gas has been carefully regulated, the inner cone burns at the top of the brass tube (*a*) and the outer cone

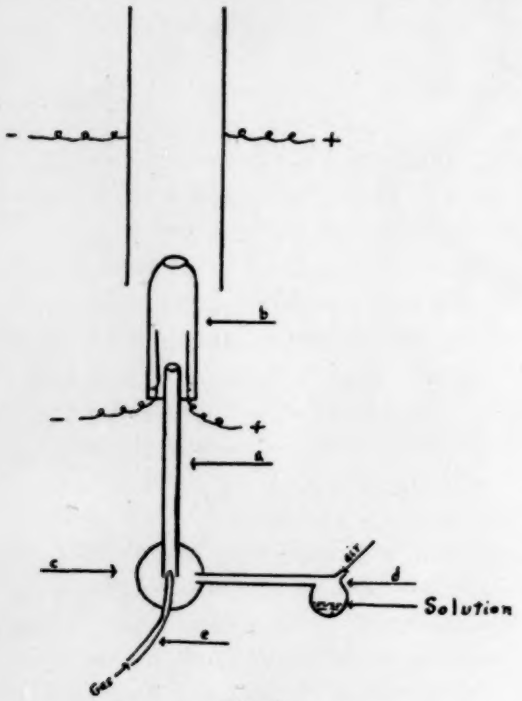


Fig. 1.

at the top of the glass tube (*b*). If no vapor is introduced, only the inner and outer cones are seen. When a vapor, Cu excepted, is allowed to enter through the inner cone, a long flame burns just above the top of that cone. This is probably the inner mantel of the Bunsen flame. In most cases there is coloration of the outer cone when vapor is introduced.

The electrical examination of the outer cone was made by placing it between two metal plates, 30 cm. square, charged by a friction machine to potentials that ranged as high as 50,000 volts. In the

investigation of the inner cone and the flames due to the vapors, two metal electrodes, 1 cm. wide, 6.5 cm. long, were placed within the glass tube on opposite sides of the inner cone, and charged by wires that passed through the plug at the bottom of the glass tube. The corners of these electrodes were rounded off so as to prevent leakage. They were so placed as to be free from contact, either with the tube or with the flame due to the vapor. Even with great precaution the strength of the field between these electrodes is small, since the conditions within the glass tube are such as favor electrical conduction. Another method of studying the electrical character of the lower cone and the vapor-flame consists in establishing a field between the tube (*a*) and the tube (*b*). This was done by placing one pole of the machine in connection with the tube (*b*), while the other was attached to the brass tube. Tests were made also in which both sets of plates were charged at the same time, to see if the electrical action of the field on the flame at the inner cone produced any change in the character of the outer cone. The spectroscopic investigation was made with a large single prism spectrometer.

(*B*) Results of the Electrical and Spectroscopic Examination.

1. *Electrical Character of the Outer Cone.*

The outer cone of the divided Bunsen flame is a hollow cone-shaped bluish flame, in its simple state. The electrical character of this simple cone was examined by observing the effect produced by an electrical field, due to the two large oppositely charged metal plates. The position of these plates, relative to the flame and to each other, was varied. At times the lower edges of the plates were about 5 cm. below the base of the outer cone; again the plates were raised and their lower edges were about 3 cm. above the base of the cone. One plate was placed close to the flame, the other was about 8 cm. distant. Then both plates were placed close to the flame, or withdrawn equally to a distance. Under none of these conditions could any electrical wandering be observed. Sometimes the cone seemed to be distorted slightly, but this may have been due to air currents.

Then the outer cone was studied in the electrical field described above for each of the following salts, Li_2CO_3, LiCl, NaCl, KCl, RbCl, CsCl, $CaCl_2$, $MgCl_2$, $SrCl_2$, $CdCl_2$ and $BaCl_2$, introduced into the cone by the Beckmann method. The results of the examination with salts of the first Mendeléeff group will be given first.

First Group. — The Li salts were introduced in large quantities in order to color the outer cone. As soon as the cone was strongly colored, the electrical examination was made. The field seemed to produce no effect upon the cone thus colored. At times a slight distortion might be noticed, but no definite wandering could be detected.

NaCl was introduced in a sufficiently large quantity to color the outer cone. At first it was thought that there was no electrical influence, but more careful observation showed a slight wandering towards the negative electrode.

Then KCl was used. The wandering of the outer cone towards the negative plate was more marked than in the case of Na. There was also a very slight bulging of the flame towards the positive plate. RbCl gave an outer cone that was drawn towards the negative plate a little more strongly than the KCl cone. When CsCl was used the outer cone was very positive, being inclined to the negative electrode at an angle of about 45°. In the case of this salt a very slight brush-like projection extending towards the positive electrode was observed.

Second Group. — The $MgCl_2$ and $CaCl_2$ outer cones show a very strong wandering towards the negative plate. For these two salts the wandering is about equal. In $SrCl_2$ the effect of the field is small; in $CdCl_2$ it increases; in $BaCl_2$ the wandering is very strong towards the negative plate, and at the same time the substance coloring the cone is drawn to the side nearest the negative plate. This effect was so strong that, frequently on the side nearest the positive plate, the cone was almost free from the Ba-salt color.

Salt Introduced into the Outer Cone Directly. — An examination of the electrical character of the outer cone was made also when a bead of salt was introduced into the outer cone directly. Several of the salts named above were tried, but the most satisfactory and definite coloration was obtained from NaCl. When a bead of this

salt was placed in the cone on the side nearest the negative electrode, the Na color was drawn towards this side, and besides there was a slight bulging of the cone towards the negative plate. This bulging was seen first near the tip of the cone, but as the field was strengthened, it was lowered and appeared as a sharp protrusion at the side of the cone. When the bead was placed on the side nearest the positive electrode, the color was carried across the top of the flame towards the negative plate and at the same time the tip of the cone was bent towards this plate.

2. *The Electrical Character of the Flame Above the Inner or So-called Carbon Cone.*

When a metal vapor was introduced into the lower cone by the Beckmann method, a flame about 10 cm. long appeared above the cone. In the examination of the electrical character of this flame, the following salts were used: NaCl, Li_2Co_3, CsCl, RbCl, KCl, $SrCl_2$ and $BaCl_2$. The first study was made by means of the two small metal electrodes within the glass tube. In all cases the wandering of this flame was strongly towards the negative plate. Further investigation was made to determine whether the wandering varied for the different salts, as was the case in the outer cone. No such variation was found. The flame bent towards the negative electrode at about the same angle which was as large as 45°, for a potential of 5,000 volts, whether Li_2Co_3 or $BaCl_2$ was used.

3. *Electrical Character of the Inner or Carbon Cone.*

When no salt was introduced, the carbon cone alone was seen at the top of the brass tube. Its electrical character was examined by means of the two small electrodes within the glass tube. When a field was established between these plates, the carbon cone was torn off the brass tube on the side towards the negative plate. It was flattened out and extended towards the negative electrode. This showed that it was strongly positive.

4. *Electrical Character of the Cones Combined.*

When the two cones were burning at the top of the glass tube, that is, when the flame is an ordinary Bunsen flame, the wandering

of this flame was towards the negative plate. It has been remarked, that the outer cone in the case of a Li-salt, showed no wandering. However, if the inner cone and the Li-flame above it were allowed to rise in the glass tube so that the top of the Li-flame touched the outer cone, immediately the outer cone began to bend towards the negative plate. This wandering continued as long as the Li-flame and the outer cone were in contact, and sometimes it has been observed that even after the Li-flame had been separated from the outer cone, the bending continued for a few seconds. It would appear that something positive was given to the outer cone from the Li-flame.

5. *Two Sets of Electrodes Combined.*

When the large outer electrodes and the two small plates within the glass tube were connected, so that one inner and one outer plate were charged positively, and the two others, negatively, the outer cone and the flame at the top of the carbon cone wandered towards the negative plates. If the inner electrode was charged positively, and an outer negatively, the salt-flame inside of the glass tube was driven away from the positive electrode, and the outer cone was drawn towards the negatively charged plate. The salts used in these investigations were $SrCl_2$ and $BaCl_2$.

6. *Phenomenon of Color Disappearance.*

This investigation was carried out by the method described in Section A. When the brass tube was charged positively and the glass tube negatively, an interesting phenomenon occurred. The carbon cone was raised above the top of the brass tube from .5 to 2 cm., this distance depending on gas pressure and air supply. The cone did not retain its original shape, but was flattened out and its edges tended upwards. At the same time the salt flame, that burned at the top of the cone before, disappeared, and only traces of color could be seen above the flattened carbon cone. This color was strongest at the cone's edges. Next the air and gas supply was so regulated that the carbon cone tended to "strike back" into the brass tube. As soon as the carbon cone was drawn so close to the top of the brass tube that any contact was made between the two, immediately a stream of color appeared above the point of contact.

When the brass tube was charged negatively and the glass tube positively, the cone was drawn down over the brass tube like a cap. The colored flame above it did not disappear as in the preceding experiment. The intensity of its light seemed to be diminished somewhat, but this may have been due to the fact that the flame was spread out and the light was not so concentrated. In these two experiments the action of the carbon cone was the same whether a salt was introduced or not.

7. *Spectroscopic Examination.*

In the spectroscopic examination of the outer cone and the flame at the inner cone for the salts NaCl, LiCl, KCl, $SrCl_2$ and $BaCl_2$, the principal series lines could be found in both the outer cone and the flame above the inner cone. Two lines of the first subordinate series appeared in the inner flame of NaCl. The carbon cone gave the band-spectrum of carbon.

Summary.

The results for the flame at the top of the inner cone are: (1) that when placed in the electrical field between the two small charged inner plates, it *always* wanders towards the negative plate, and that its inclination is about the same, for the same strength of field, irrespective of the salt used; (2) when studied in a field set up between an inner electrode positively charged, and an outer electrode negatively charged, it is repelled by the positive plate; (3) as soon as this flame comes in contact with a neutral outer cone, wandering towards the negative plate occurs in this outer cone. From these facts we may conclude that this flame is always electrically positive.

The results for the inner or carbon cone are: (1) it is drawn very strongly to the inner negative plate; (2) it is repelled by the brass tube when this tube is charged positively, and it is attracted to this tube when negatively charged. Hence the inner or carbon cone is always positive.

The results for the outer cone are: (1) for the five elements of the first Mendeléeff group, that were studied, the electrical wandering, when present, is towards the negative plate, and increases with the atomic weight of the metal. Li shows no wandering; the wander-

ing begins with Na, increases for K and Rb and reaches a maximum for Cs; (2) for the elements studied of the second Mendeléeff group, there is always electrical wandering towards the negative plate, but there is no relation between atomic weight and electrical wandering. $MgCl_2$ and $CaCl_2$ show a very strong wandering towards the negative plate; for $SrCl_2$ the wandering is small, for $CdCl_2$ it is larger than it is for $SrCl_2$, but smaller than for $MgCl_2$ and $CaCl_2$, for $BaCl_2$ the wandering is greatest.

The results for the spectroscopic examination are: (1) the principal series lines come from the flame above the carbon cone, which flame is always strongly positive, whatever salt is used. They come also from the outer cone, which is neutral, slightly positive or strongly positive according to the salt used; (2) the first subordinate series lines come only from the positive salt-flame, which is just above the inner or carbon cone for all the salts; (3) the so-called band-spectrum of carbon arises from the inner cone, which is always strongly positive.

(*C*) Discussion of Results.

The primary object of the investigation described in this paper was to study the electrical character of the source of the light radiation. As the examination advanced, it became more and more evident, that although we may study the character of the source of the light radiation experimentally, yet in the interpretation of results, account must be taken of processes that are possibly closely connected with the electrical phenomenon. A complete analysis and interpretation of the results recorded in this paper would require a fuller knowledge than we have at present, of the chemical and thermal processes involved in the divided Bunsen flame. In the consideration of the chemical or other processes that occur in this flame, where it has been necessary to take account of such processes, the opinions and theories of other investigators concerning them have been used.

The electrical wandering of the outer cone for different elements of the first Mendeléeff group is progressive like the atomic weights and electrical conductivity, and bears some relation to these properties. In the following table atomic weight, electrical conductivity

and electrical wandering are given. The bending of the cone from the vertical is given in degrees. The electrical conductivity for these different metal vapors is the conductivity of a flame into which these different vapors have been introduced.

	Li.	Na.	K.	Rb.	Cs.
Atomic weight.....	7	23	39	85	132
Electrical wandering.....	0°	9°	20°	22°	45°
Electrical conductivity.....	2.5	8.5	64	82	116

In the elements studied for the second Mendeléeff group, elements of high and low atomic weights give the larger wanderings.

	Mg.	Ca.	Sr.	Cd.	Ba.
Atomic weight.....	24	40	87	112	137
Electrical wandering.....	36°	36°	18°	27°	45°
Electrical conductivity...			Not known.		

In using the Beckmann method, metal vapor enters the inner cone. To suggest a possible explanation for the variation of electrical wandering in the outer cone, we must inquire into the changes, chemical and electrical, which the metal vapor undergoes after it enters the inner cone. What electrical character has it when it first enters the inner cone? This question, it seems, is answered by the phenomena of the disappearance of the salt-flame when the glass tube is negatively charged and the inner cone driven up from the top of the positively charged brass tube. An explanation of this occurrence is that the metal vapor is strongly positive, and that when it reaches the top of the brass tube, it is drawn towards the negatively charged brass tube, and thus prevented from entering the inner cone. This explanation is supported by the fact that whenever coloring is seen in the inner cone it appears at the extended edges, as if some metal vapor passing beneath the flattened cone at times came in contact with those edges. Again, as soon as the inner cone came in contact with the brass tube there was a sudden appearance of color as if the vapor was continually passing over the upper edges of the brass tube.

According to Fredenhagen, an oxidation process occurs in the flame above the inner cone, the oxidation continues in the outer cone, whenever the color of that cone corresponds to the elements used. While this vapor is undergoing the oxidation process in the flame above the inner cone it is still very positive and equally so for

all the salts studied in both groups, as is evident from the equal wanderings of all salt-flames. But in the outer cone it has changed, being neutral, slightly or strongly positive according to the element introduced into the inner cone. During this oxidation process, therefore, Li becomes electrically neutral, Na, K and Rb become less strongly positive, while Cs apparently remains as strongly positive as before.

It might be suggested that while the metal is uniting with the oxygen it is gradually losing its positive character, and that when it has been brought to the state of a complete oxide it has become electrically neutral. In the last stages of this oxidation process it may be possible that the neutral effect has been brought about before the oxidation process has been completed. This would explain the neutral character of Li in the outer cone. In Cs or Ba the oxidation process may take place much more slowly, and the positive charge of the metal vapor would not have been neutralized when the vapor of the elements would reach the outer cone.

An explanation of the neutralization process may be offered on the ground that there are free negative electrons present in the two cones and the salt-flame. These electrons would unite with the positive metal ions that enter through the brass tube. These electrons may be present in much larger numbers in the flame and cone within the glass tube than in the outer cone.

Such a supposition would explain the apparent discrepancy between Lenard's results, that the outer edge of the Bunsen flame showed no wandering when a NaCl bead is placed in the edge, and the wandering effect observed when a bead of NaCl is introduced directly into the outer cone. In Lenard's experiment with the ordinary Bunsen flame, the cones being so closely united, the free negative electrons in the inner part of the flame would pass to the outer edge more readily than when the cones are separated as in the divided Bunsen flame. Therefore the outer cone in the ordinary Bunsen flame would contain a larger number of free electrons than the outer cone of a divided Bunsen flame, and we would expect the neutralization of a vapor to take place more quickly in the former than in the latter.

The question arises, how can the relation between electrical

wandering, atomic weight and electrical conductivity be explained? A possible explanation could be offered if it be supposed that the free negative electrons are present in the two cones as stated above, and that these electrons are connected in some way with the conduction of electricity by flames. These assumptions together with the suggestion made to explain the neutralization of a metal vapor while passing through the cones may give some answer.

In the first Mendeléeff group the electrical wandering increases with atomic weight. This means that the greater the atomic weight of an element the longer a metal remains positive, and this occurs either because the electrical force acting between electrons and positive ions decreases as the atomic weights of the metals increase, or because the heavier the element, the larger the number of electrons necessary to neutralize it. This would give an explanation of the observed relation between atomic weight and electrical wandering.

Now, as has been supposed, the more neutral the outer cone, the less the number of free negative electrons present in the cone. The presence of a large number of negative electrons may give rise to that bulging or brush-like effect which has been observed in certain outer cones. But if the conduction of electricity depends upon these electrons then the greater their number in a cone the better conductor the cone will be, therefore, the more positive the cone, *i. e.*, the greater number of electrons in it, the better a conductor it will be. Then, the more positive the outer cone, *i. e.*, the greater the atomic weight of the metal from which the outer cone comes, the better it conducts. These considerations would give an explanation of the observed relation between electrical conductivity and electrical wandering.

The most important result of this investigation is the demonstration of the presence of principal series lines in sources whose electrical character presents qualitative differences. This fact is brought out most clearly in the case of Li. The Li outer cone is electrically neutral and principal series lines are obtained from it; the Li flame above the inner cone is always positive and principal series lines are obtained from it also. Therefore the principal series lines of Li arise from a positive or neutral source.

For Na, K and Rb, the outer cone contains some positive matter. This means that for these metals, either the positive metal ions have not been fully neutralized as yet, or that all the positive metal ions of an element are not neutralized with the same readiness and therefore in this outer cone we may have positive metal ions and neutral particles as well. The latter explanation, namely, that there are positive and neutral light-giving particles in the outer cone seems to be the more probable in view of the fact that only part of the cone appears to be affected by the electrical field, whereas part is not influenced by the field and therefore is neutral. When the outer cone is strongly positive, as with Cs for example, there are few if any neutral particles in this cone, and the light-emission of the outer cone comes in great part, if not wholly, from a positive source.

The value of this result, namely, that principal series lines come from a neutral as well as from a positive source, is that it helps to show that the results of Lenard and Stark in regard to the electrical character of the source of principal series lines are not really in disagreement; that the different conditions under which they worked gave them really only apparently different results as to the electrical character of the source. In the investigation described above conditions are such that the results of both Stark and Lenard are obtained. The conditions of investigation might be such that the results of Stark, Lenard and Thomson could be obtained simultaneously, *i, e.*, we could have principal series lines arising from positive, negative and neutral sources.

The most obvious inference is that, at least for principal series lines, the source need not be always positive or always neutral or always negative but that the source may be positive or negative or neutral, depending upon the conditions under which emission is brought about. The electrical character of the source of the principal series lines seems to be an accidental rather than an essential condition.

The investigation shows further that the subordinate series lines have a positive source as found by Stark and Lenard.

The band-spectrum, so far as studied in this investigation, *i. e.*, for carbon, arises from the inner or carbon cone, *i. e.*, from a posi-

tive source. Thomson found the band-spectrum for carbon arising from a negative source. Stark found the source for the band-spectrum of hydrogen and other elements to be neutral, and concluded that the source of the band-spectrum is neutral. Here as in the case of principal series lines, the band-spectrum seems to be due to sources that may be positive, negative or neutral in electrical character. Here also we may make the same inference as for principal series lines, namely, that the electrical character of the source of the band-spectrum is accidental and not a necessary condition.

I take this opportunity of acknowledging my obligation to Drs. Griffin and Shea for continued suggestion and assistance throughout this investigation, a considerable portion of which has been conducted in collaboration with the latter.

PHYSICAL LABORATORY,
CATHOLIC UNIVERSITY OF AMERICA,
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THE NOZZLE EXPANSION OF AIR AT HIGH PRESSURE.[1]

BY W. P. BRADLEY AND C. F. HALE.

INTRODUCTION.

THE problem of reducing the permanent gases to the condition of static liquids by a continuous process and on a large scale was solved in 1895 by Linde and by Hampson. Their liquefiers differ in construction, but in each of them the gas is cooled to the liquefaction point by expansion through a throttling valve or nozzle.

Two views are held at the present time as to the cause of the absorption of heat during this method of expansion. Linde[2] explains it by the Joule-Kelvin effect, and his view appears to be accepted by the majority of writers on this subject. According to this view the heat is absorbed in overcoming molecular attractions which exist in the gas at the higher pressure. The formula commonly given is

$$d = 0.276\,(p_2 - p_1)\left(\frac{273}{T}\right)^2,$$

derived from the results of Joule and Kelvin,[3] in which d is the cooling effect in degrees, p_2 and p_1 are the initial and final pressures in atmospheres, and T is the initial temperature on the absolute scale.

This view has been vigorously attacked by Pictet,[4] who insists that the heat absorption is to be accounted for by the *external* work of overcoming the pressure which prevails in front of the valve. In

[1] For generous support in the prosecution of this inquiry we are indebted to two grants from the Hodgkins Fund of the Smithsonian Institution.

[2] Wiedemann's Annalen, *57*, 328, 1896. Also abstract of paper by Schrötter, Sci. Am. Supplement, December 21, 1895.

[3] Philosophical Transactions, *152*, 579, 1862.

[4] Zeitschrift für comprimirte und flüssige Gase, 7,1, ffg., 153, ffg., 1903; *8*, 8, fig., 1904; *9*, 51 passim to *10*, 110, 1905–1907.

the Hampson liquefier and in the older single-circuit liquefier of Linde, this work consists merely in pushing back the external atmosphere. Pictet computes the cooling effect by means of the formula[1]

$$d = \frac{T\left(1 - \frac{1}{p}\right)10.33}{273 \times 1.293 \times c \times J + 10.33},$$

where d and T have the same significance as before; p is the initial pressure in atmospheres; c is the specific heat of air at constant pressure; and J is the mechanical equivalent of heat.

The essential differences between these two formulas are obvious. If the view of Linde is correct, the cooling effect is a linear function of the difference in pressure on the two sides of the valve. Thus, for air at zero, a difference of 100 atm. corresponds to a fall of 27.6 degrees; a difference of 200 atm. to a fall of 55.2 degrees. Where the initial pressure is high and the final pressure is one atmosphere, the latter indeed may be ignored, and the cooling effect may be considered proportional to the initial pressure.

According to Pictet, on the other hand, air at zero will fall 60.7 degrees when expanding from 101 atm. to one atmosphere, as against 61 degrees when the initial pressure is 201 atm. Pictet indeed particularly emphasizes the view that pressures higher than 25–30 atm. neither can nor do have any considerable influence in the way of increasing the cooling effect unless the liquefier is grossly deficient in interchanger surface.[2] It is clear of course that if the expanded air passes over the coils of the interchanger without reaching the temperature of the inflowing air of high pressure, the defect may be remedied more or less by the use of a higher initial pressure, whereby the same mass of air will flow more slowly down the tubing to the expansion valve.

The divergence of the two views is equally noteworthy as regards the effect of initial temperature. According to Linde, the cooling effect at the valve *increases* rapidly as the initial temperature falls. Thus, for a fall of pressure of 200 atm. at zero it is 55.2 degrees. At $-82°$ it is 112.2 degrees, or enough to bring the air to the

[1] In the original formula the cooling effect is represented by θ instead of d.

[2] *Loc. cit.*, 7, pp. 40–41.

liquefaction point at one atmosphere. According to Pictet's formula it *decreases* for lower initial temperature. Thus, it is 61 degrees if the initial temperature is zero, but only 42.7 degrees if the initial temperature is — 82°. The final temperature in the latter case is — 124.7°, which is 70 degrees distant from the liquefaction point at one atmosphere.

It may be remarked in passing that according to Pictet's view it is not easy to account for the production of liquid air at all when a liquefier is fed with air under a pressure above the critical pressure. According to his value of *d*, air at 55 atmospheres must be cooled to — 172.3° before the expanded air can reach the liquefaction point at 194.5°. If the pressure is 200 atm. the air must still be cooled to — 172°. In either case, as the critical pressure is 51–53 atm. (*loc. cit.*, p. 19), the air would be completely liquefied before it reached the expansion valve (p. 17). As liquid while passing the valve can absorb no heat (p. 22), the functioning of the liquefier would cease (p. 23) until the temperature of the air just before expansion should rise above the critical temperature (= — 141°, p. 8). Then the heat absorption would begin again while the gas passed the valve, but would cease at once as soon as the temperature fell again below the critical temperature. Apparently an interchanger could functionate only so long as the initial temperature remained above — 141°. But if — 141° is the lowest effective initial temperature, the lowest obtainable final temperature according to Pictet is — 170.5° at 201 atm., or — 170.1° at 55 atm. To produce liquid at one atmosphere, about 25 degrees more are required, and these could never be realized so long as the initial pressure was higher than the critical pressure, *i. e.*, as long as further cooling would result in complete liquefaction inside the pipes.

Although it has been shown, contrary to the view of Pictet, that increase of pressure has a profound influence on the yield of a liquefier, an influence which cannot be accounted for on the basis of inadequate interchanger surface;[1] and that the air at 200 atm. has *not* reached its critical temperature before expansion,[2] but that its temperature is certainly not lower than — 100° when liquid air

[1] Bradley and Rowe, PHYS. REV., *19*, 339, 1904.

[2] Bradley and Hale, PHYS. REV., *19*, 391, 1904. *Cf.* also Schröter, *loc. cit.*

is collecting in the reservoir at atmospheric pressure, the general subject seemed of sufficient importance to call for a more detailed experimental examination.

Experimental Part — The Apparatus.

Measurement of Pressures. — Pressures were measured by a metallic gauge with a seven and one half inch dial. This was graduated to 4,000 lbs. in divisions of ten pounds. When the lag of the pointer was corrected by tapping upon some effective spot of the casing, it was possible to read to single pounds. The gauge was calibrated with care by the use of a frictionless hydrostatic balance with lever arm, pan and weights.

Measurement of Temperatures. — Four platinum resistance thermometers were used, one in the high pressure circuit just above the valve, and three in the expanded air at different distances from the valve, in a manner which will be set forth below in detail. They were made of pure insulated platinum wire, 0.0798 mm. in diameter and 35–40 cm. in length. The wire was wound upon the end of a heavy copper lead, which in addition to its two-ply cotton insulation was wrapped with adhesive insulating tape. The latter helped to keep the turns of the platinum wire in place. One end of the platinum wire was soldered to the tip of the copper lead upon which it was wound. The other end was soldered to a similar copper wire which served as the other lead.

Resistances were measured by means of a Wheatstone bridge and a D'Arsonval galvanometer. The maximum sensitiveness was about .01 ohm, corresponding to 0.3°. This was quite sufficient, inasmuch as the temperatures to be read could scarcely be held constant to less than that amount.

The thermometers were carefully calibrated in pure cracked ice, in a carbon dioxide-ether mixture, and in pure liquid oxygen. The oxygen was prepared from sodium peroxide and water, and was purified by passing it through a saturated potassium hydroxide solution, through conc. sulphuric acid, previously boiled to expel air, and through phosphorus pentoxide. Great care was taken to remove traces of air from the apparatus. The gas was condensed by means of liquid air boiling under atmospheric pressure, and was

perfectly clear and limpid. When enough liquid oxygen had accumulated to cover the thermometer, the liquid air bath was lowered and the oxygen was allowed to distil away under atmospheric pressure. To avoid superheating, pure oxygen gas was allowed to bubble through the liquid from a capillary tube. Allowing for the resistance of the copper leads and for the barometer readings, and assuming that the normal boiling point of oxygen is $-182.8°$,[1] and that of the carbon dioxide-ether mixture is $-78.34°$,[2] the curve of resistance was practically rectilinear. As the error involved in assuming the curve to be rectilinear from zero to $-78.34°$, and from $-78.34°$ to $-182.8°$ respectively was entirely negligible, this course was adopted.

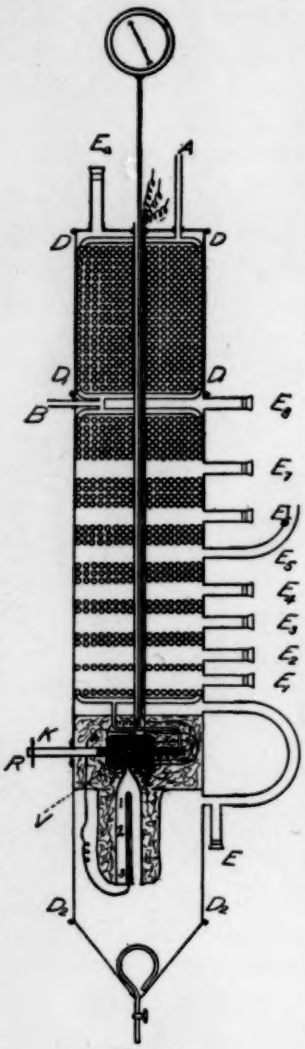

Fig. 1.

The Interchanger.— Previous experience had demonstrated that an interchanger, such as is found in all air liquefiers, would be the most convenient method of securing constant low temperatures over a wide range. The plan was the simple one of constructing such an interchanger in sections, suitably spaced from one another vertically, and provided with a corresponding number of exhaust pipes for the expanded air. The arrangement is illustrated in Fig. 1.

The interchanger consisted of two tubes of equal length, wound in parallel so as to save friction. The tubing was of seamless-drawn copper, of 4.8 mm. internal diameter and 0.8 mm. wall. The discs when wound were about 11 cm. in diameter. A

[1] Travers, Sentner and Jacquerod, Zeitschrift für physikalische Chemie, *45*, 416, 1903.
[2] Holburn, Annalen der Physik (4), *6*, 245, 1901.

space of 1.5 mm. was left between adjacent turns of tubing in each disc, and a similar space between adjacent discs in each section. There were nine sections in all, containing respectively 1, 1, 2, 2, 3, 3, 4, 6 and 15 discs of tubing, reckoned from the valve upward. The space between adjacent sections was about 3 cm.

The interchanger was wrapped in three layers of flannel, and was provided with a very snugly fitting case of tin, the lower conical end of which served as a reservoir for liquid air when the temperature was low enough to produce it. At the side of the casing, at a level corresponding to the spaces between the sections of the interchanger, eight wooden outflow tubes, E_1–E_8, were attached, the flannel wrapping of the interchanger being suitably cut away at the inner end of each. In the cap at the top was another outflow tube E_9 corresponding to the usual one in an air liquefier.

For most of the work, except that at low pressures, the thick upper section of the interchanger was superfluous, and accordingly provision was made for cutting it out from the air circuit when desired, and for the introduction of the compressed air at B, between it and the next lower section. When B served as the inlet, A was capped, and vice versa.

The casing was made in two sections, joined at D_1D_1 by bolted flanges with rubber packing. By unbolting at D_1D_1 and withdrawing the valve stem R, the interchanger and valve could be lifted out of the lower section of the case, thus greatly facilitating adjustments or necessary repairs. In a similar way the conical base of the casing could be removed at the joint D_2D_2, as well as the cap at DD. The casing was heavily wrapped with hair felt for the sake of insulation from the heat of the room.

When the air entered at A, for example, it passed through the entire length of the tubing of the interchanger to the valve V. After expansion through the valve it passed out of the case, either at E, without any contact with the interchanger, or at some one of the other exhausts, E_1–E_9, after passing over one or more sections of the interchanger. Except for a circumstance which will be explained later, only one exhaust was opened at a time.

In passing downward through the interchanger, parallel-wound though the latter was, the air met with a certain amount of frictional

resistance. For this reason the pressure gauge was connected with the system at a point as near the valve as possible. This connection was made through the core of the interchanger, as may be seen from the figure.

The Valve. — The greatest care was observed in the construction of the valve, with a view to preventing interchange of heat between the air before, and the air after, expansion. A valve constructed of metal, as is usual in air liquefiers, must itself act in some degree as an interchanger, owing to the conducting power of its walls. In order to avoid this source of error as far as possible, the valve walls and seat were made of vulcanite. The details are shown in Fig. 2.

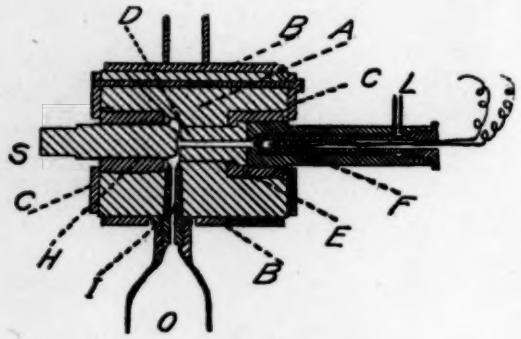

Fig. 2.

A is a vulcanite cylinder, 5 cm. long and 4 cm. in diameter. In order to reinforce it against bursting, it is surrounded with a cylindrical brass sleeve *B*, which is cut horizontally at a point not shown in the figure, and is provided with flanges in such a way that it can be bolted around the vulcanite as tightly as may be necessary. Incidentally, it is this brass sleeve which holds the valve in place with reference to the interchanger, for it is attached to the lower end of the tubular core of the latter. For longitudinal reinforcement, circular brass plates *CC* are provided at the ends of the vulcanite, and these are held firmly together and against the ends of the vulcanite by bolts, one of which is shown. The plates are not in metallic contact with the sleeve.

The valve seat *D* is a separate piece of vulcanite, fitting snugly into the core of the main block. It is carried by the brass sleeve

E, which backs against one of the reinforcing plates for greater strength, and is held firmly in place in the sleeve by the hollow brass screw-plug *F*, which will be described presently.

The valve stem *S* is of brass. In preliminary experiments we used one of vulcanite for the sake of better insulation, but it proved very unsatisfactory. The pressure upon the stem, while not excessive, is considerable, and the threads are apt to wear. If the stem fits snugly into its sleeve, it is apt to stick fast at low temperatures, with the attendant danger of breaking under torsional strain. If it turns more freely, air is liable to leak by it into the space around the valve box. Probably the danger from conduction in a metallic stem is very slight, for the passage of heat into it from the parts in contact with the unexpanded air is a very roundabout one indeed. For the sake of greater safety, the stem plays in a brass sleeve *H*, which backs against the end plate, and is pinned to prevent its turning with the stem. The continuation of the stem (*R*, in Fig. 1) is of wood, and passes through a soft rubber disc in the interchanger case at *K*. A hollow screw-plug *I* conducts the expanded air from the valve cavity to the outflow tube *O* which carries three of the thermometers.

Before the valve was used, it was thoroughly tested for strength and tightness. At the conclusion of the experiments it was in as perfect condition as at the beginning.

The Arrangement of the Thermometers. — The brass screw-plug *F* (Fig. 2) consists of three parts — an outer cylindrical shell, a thin-walled thermometer pocket, with a flange at the open end, and a binding nut at the outer end to hold these together in place. On the inner side of the flange of the thermometer pocket was a fiber washer to make the joint tight. Air from the interchanger enters at *L* and passes over the entire length of the thermometer pocket into the valve seat *D*. The internal diameter of *L* and of *D* is 2.18 mm. and the annular space between the thermometer pocket and its case was so calculated that the area of its cross-section was the same as that of *L* and *D*.

The thermometer for measuring the initial temperature was placed in the inner end of the pocket, and was cast firmly in place by pouring in melted paraffin. The lead wires passed out through the

binding nut and up through the core of the interchanger to the bridge and galvanometer, as shown in Fig. 1.

The temperature after expansion was measured by three thermometers similarly enclosed in a single pocket, each separated from its next neighbor by a space of 4 cm. The general arrangement of these also can be seen in Fig. 1. The pocket is provided at its lower end with three radiating slitted straps, as illustrated in Fig. 3, by means of which it can be bolted firmly to the flanges of outflow tubes of different diameters. In the figure, P is the mouth of the pocket, SSS are the straps, F is the flange at the base of the outflow tube, and E is the open space through which the exhaust escapes into the casing of the interchanger.

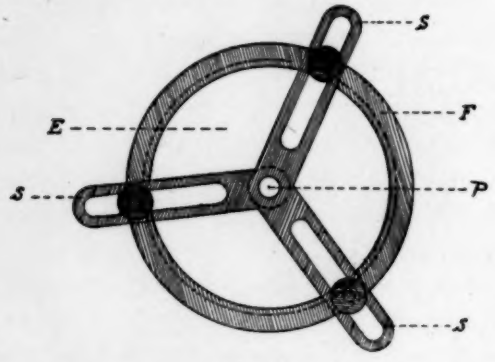

Fig. 3.

The reason for the use of three thermometers at this point was the following. Joule and Kelvin[1] found that when air was allowed to expand through a single orifice, its temperature was lower close to the orifice than at a distance of a quarter of an inch. Our own preliminary experiments confirmed this observation. In fact when a mercury thermometer was thrust up into the outflow tube toward the small orifice at the top, it registered lowest when the bulb was in the position corresponding to that which is the normal one for the ball in a ball-nozzle — a position which is very close to the orifice, and in which the thermometer bulb is held with some force in a condition of equilibrium by the action of the air current. If the

[1] Philosophical Magazine (4), *4*, 481, 1852. *Cf.* Travers, "Study of Gases," pp. 189–90.

bulb was pushed out of this position and nearer to the orifice, the temperature rose quickly. Also if it was urged towards the walls of the outflow tube, or drawn away from the orifice, the temperature rose, but not so rapidly. In any part of the tube more than two inches from the orifice the temperature registered was practically constant. Three thermometers, spaced as shown in Fig. 1, gave us therefore not only a record of the final temperature of the exhaust, but also some idea of the process by which that final temperature was reached.

Insulation of the Valve. — Careful consideration was given to the insulation of the valve from its own exhaust. It is clear that if any part of the latter plays around the valve, as it would be allowed to do in a liquefier, there could be no guarantee that the readings of the initial temperature were not affected by it. Accordingly, both the valve and its exhaust were sheathed with a compact layer of hair felt, which was held in place by means of adhesive tape, so wound as to be practically air tight for small differences of pressure. Then other layers of felt and adhesive tape were applied, until a drum-shaped cylinder was built up, of the same diameter as the casing of the interchanger. This drum was wrapped with flannel like the interchanger, until it fitted the casing so tightly that air currents were prevented from passing by it. As it was now impossible, inside the casing, to bring the expanded air past the valve to the interchanger in the ordinary way, a well-insulated by-pass was attached outside, as shown at the right in Fig. 1.

The Air Supply. — Air was delivered to the interchanger from a four-stage Norwalk compressor at a maximum rate of about 20 cubic feet per minute. As any deposition of solid matter in the valve, or in the tubes immediately adjacent, would alter the available diameter of the respective passages and so not only make more difficult the task of keeping the valve in proper adjustment, but also, it was feared, occasion abnormalities in the cooling effect at the valve because of changes in the relative velocities of the air before and after expansion, the air was purified very carefully by passing it through strong steel cylinders containing sticks of solid potassium hydroxide and well screened granular calcium chloride respectively. No difficulty was experienced in the experiments

from the formation of solid, except when the initial or final temperature was in the vicinity of zero or — 78°. The resulting annoyance even then was trifling when a normal amount of air passed the valve, except at the beginning of a run. When less air than the normal quantity was used, for a purpose to be explained later, it was often necessary to avoid these points entirely on the temperature curves. It was clear that the purification was not an absolute one.

It was never difficult to tell when the conditions at the valve were abnormal in this regard. The fact was heralded by slight but spasmodic motions of the gauge pointer a considerable time before any change could be detected at the galvanometer.

Experience has shown that the purification of the air supply is very greatly simplified if the exhaust from the expansion valve is delivered again into the intake of the compressor, instead of using steadily new air from outside as is often done. Accordingly the exhaust was taken by means of a flexible rubber hose from the exhaust pipes E–E_9 to a forty gallon reservoir, which communicated directly with the intake of the compressor and also with the external air. In this manner the exhaust was not only saved but was maintained at atmospheric pressure. In the event of perfect functioning of the compressor and of perfect adjustment of the expansion valve, the air circuit was practically, though not actually, a closed one,— unless indeed air were being withdrawn from the circuit by liquefaction.

Method of Operation.— At the beginning of a run warm air was blown through the whole interchanger, at comparatively low pressure and with the valve wide open, in order to remove any traces of moisture left from the preceding run. During this period, the exhaust was allowed to escape from E, so as not to cool the interchanger. The valve was then shut, until the pressure reached the desired amount, when it was opened again sufficiently to deliver as nearly as possible the exact amount of air which was being pumped by the compressor. The exhaust meanwhile was delivered through that one of the wooden tubes E_1–E_9 which experience had shown would carry the valve temperature down to the desired region.

During the cooling of the interchanger and the consequent con-

traction of the air within it, it was necessary to adjust the valve frequently in order to maintain constant pressure. On the other hand, when thermal equilibrium was reached, the valve could often remain at a single adjustment for periods of twenty minutes or half an hour without sensible change in the pressure.

The time required for the establishment of thermal equilibrium varied of course with the proportion of the interchanger which was thrown into the circuit. Without the interchanger, fifteen minutes would usually suffice. When the entire interchanger was in action an hour might be required. For this reason it was found of great advantage in the final series of experiments, to precool the air supply, when necessary, by means of ammonia refrigeration. To this end the air from the purifiers passed through one half of a double copper coil, while liquid ammonia evaporated at constant pressure through the parallel half, which was soldered coaxially to the first. In this way, by the use of a throttling valve in the ammonia circuit, the temperature of the air supply could be shifted in a minute or two to any desired point, from about $-30°$ to the temperature of the room. In addition to the saving of time thus effected through the use of a minimum of interchanger surface, the precooling of the air supply in this way facilitates the attainment at the valve of any specific temperatures which may be desired, instead of a certain number of temperatures spaced from one another in correspondence with the respective cooling effects of the individual sections of the interchanger.

In order to economize time still further, especially towards the end of a period of thermal adjustment, when the process is always slowest, the practice was to choose that one of the outflow tubes E_1–E_9 which would give a final temperature somewhat too low; then, when the desired temperature was reached, to check further progress downward by switching out a small portion of the exhaust at E, so as to remove it entirely from action on the interchanger. By manipulating a suitable throttling valve at this point, the proper proportion could be easily hit upon experimentally. Of course this portion of the air was led back into the compressor like the rest.

A sample page from the original note-book will make these matters clear. It should be noted that temperature readings were usually not recorded at all until equilibrium was near at hand.

TABLE I.

Record of Observations on March 7, 1907.

Time.	Resistance —Inflow.	Resistance—Outflow.			No. Sections Interchanger.	Pressure (Gauge).
		No. 1.	No. 2.	No. 3.		
Hr. Min.	Ohms.	Ohms.	Ohms.	Ohms.		Lbs.
3 30	7.70	4.79	4.79	5.15	1	3,000
35	7.64		4.73	5.07		
40	7.61		4.70	5.06		
45	7.58		4.67	5.02		
48	7.58	4.86	4.66	5.01		
50	7.58	4.86	4.66	5.01		
4 20	6.68		3.40	3.66	3	3,000
25	6.67	3.51	3.38	3.63		
30	6.66	3.50	3.35	3.61		
33	6.66	3.50	3.35	3.61		
4 55	5.70	1.86	1.78	1.95	6	3,000
5 00	5.70	1.86	1.78	1.95		
5 10	5.40		1.75	1.87	8	3,000
15	5.37	1.83	1.74	1.87		
20	5.37	1.83	1.74	1.87		
		Throttle opened a little.				
25	5.43		1.74	1.87		
28	5.43	1.83	1.74	1.87		
		Throttle opened more.				
35	5.57	1.83	1.74	1.87		
40	5.57	1.83	1.74	1.87		

The foregoing table represents the way in which the results of different initial temperatures were obtained while the pressure remained constant. It appeared later that still less time was consumed, on the whole, when a series of readings was based on a constant amount of interchanger surface, with varying pressure. Table II. illustrates this method.

The results obtained by these two methods were entirely concordant.

RESULTS.

Table III. contains the results of our final series of experiments. This series was made after the lapse of more than a year and a half spent in perfecting the apparatus and in acquiring facility and precision in its handling. The series itself required the greater part of two months for its completion. Typical readings were checked repeatedly at the beginning of the runs on different days.

TABLE II.

Record of Observations on March 19, 1907.

Time.	Resistance —Inflow.	Resistance—Outflow.			No. Sections Interchanger.	Pressure (Gauge).
		No. 1.	No. 2.	No. 3.		
Hr. Min.	Ohms.	Ohms.	Ohms.	Ohms.		Lbs.
2 55	7.66	5.73	5.48	5.90	4	1,500
3 00	7.60	5.67	5.41	5.82		
3 03	7.55	5.61	5.36	5.76		
06	7.55	5.61	5.36	5.76		
3 30	7.25	4.92	4.69	5.05	4	2,000
35	7.24	4.88	4.66	5.03		
40	7.22	4.88	4.65	5.00		
45	7.22	4.88	4.65	4.98		
48	7.22	4.87	4.63	4.98		
4 00	7.09	4.38	4.17	4.50	4	2,500
05	7.06	4.38	4.17	4.48		
10	7.02	4.34	4.13	4.42		
12	7.02	4.32	4.12	4.43		
15	7.02	4.34	4.13	4.43		
16	7.02	4.34	4.13	4.43		

Five different pressures were employed, viz., 1,000, 1,500, 2,000 2,500 and 3,000 lbs. gauge. There was a certain amount of back pressure caused by the friction of the exhaust as it passed through the coils of the interchanger, and through the pipes which conveyed it to the reservoir where atmospheric pressure prevailed, as described above. It amounted to less than 0.05 per cent. of the total pressure difference. This is entirely negligible in comparison with the unavoidable errors in reading the gauge and the thermometer resistances, and was left out of account.

The initial temperature varied from + 20° to — 120°.

It will be observed that the three thermometers always differ from one another for a given initial temperature, except at the temperature of liquefaction. The thermometer nearest the valve, no. 1, reads lowest, and that which is farthest away, no. 3, reads highest; and in general the difference between nos. 1 and 2 is greater than between nos. 2 and 3. These differences are not due to defective insulation around the outflow tube which contains the thermometer pocket, for they become *greater* when the general temperature of the blast is higher. Defective insulation would produce exactly the

TABLE III.

Final Results.

Pressure.	Thermometer Resistances (Corrected).				Temperatures.			
	Inflow.	No. 1.	No. 2.	No. 3.	Inflow.	No. 1.	No. 2.	No. 3.
Lbs.	Ohms.	Ohms.	Ohms.	Ohms.	Deg.	Deg.	Deg.	Deg.
1,000	9.12	7.46	7.21	7.79	+ 9.8	− 11.0	− 6.9	− 6.0
	8.19	6.54	6.30	6.80	− 17.1	− 40.8	− 37.9	− 37.4
	7.58	5.92	5.69	6.16	− 34.7	− 60.8	− 58.8	− 57.7
	6.75	—	4.85	5.25	− 58.7	—	− 87.4	− 86.4
	6.57	4.87	4.68	5.05	− 63.9	− 94.5	− 93.0	− 92.6
	6.10	4.27	4.09	4.43	− 77.4	−113.6	−112.7	−111.8
	6.04	4.19	4.02	4.34	− 79.1	−116.7	−115.0	−114.6
	5.59	3.61	3.46	3.75	− 91.8	−134.3	−133.7	−132.9
	4.92	2.53	2.43	2.63	−110.6	−168.8	−168.1	−167.6
	4.59	1.75	1.67	1.89	−119.9	−193.6	−193.5	−190.5
	4.53	1.74	1.65	1.78	−121.6	−193.9	−194.1	−193.9
1,500	9.31	7.43	7.19	7.77	+ 15.3	− 11.9	− 7.5	− 6.7
	8.61	6.72	6.48	7.00	− 4.9	− 34.9	− 31.8	− 31.1
	8.20	6.27	6.05	6.53	− 16.8	− 49.6	− 46.5	− 46.0
	7.54	5.58	5.35	5.78	− 35.8	− 71.8	− 70.4	− 69.7
	6.71	4.56	4.41	4.75	− 59.8	−104.4	−102.0	−101.9
	5.84	3.32	3.19	3.44	− 84.8	−143.8	−142.7	−142.5
	5.34	2.42	2.38	2.58	− 98.8	−172.4	−169.8	−169.1
	5.21	2.14	2.11	2.29	−102.4	−181.2	−178.8	−178.1
	5.06	1.75	1.78	1.93	−106.7	−193.6	−189.8	−189.3
	5.05	1.74	1.65	1.82	−107.0	−193.9	−194.1	−192.7
	5.03	1.74	1.64	1.78	−107.5	−193.9	−194.5	−193.9
	4.97	1.73	1.64	1.77	−109.2	−194.2	−194.5	−194.2
	4.89	1.72	1.64	1.77	−111.5	−194.5	−194.5	−194.2
2,000	9.46	7.42	7.15	7.74	+ 19.7	− 12.3	− 8.9	− 7.6
	8.62	6.47	6.25	6.76	− 4.6	− 43.0	− 39.7	− 38.7
	7.34	5.00	4.81	5.20	− 41.6	− 90.4	− 88.7	− 87.9
	6.84	—	4.16	4.50	− 56.0	—	−110.4	−109.6
	6.16	3.35	3.21	3.46	− 75.7	−142.8	−142.1	−141.9
	5.79	2.75	2.62	2.83	− 86.2	−161.8	−161.7	−161.4
	5.36	1.76	1.81	1.98	− 98.2	−193.3	−188.8	−187.8
	5.29	1.73	1.67	1.81	−100.2	−194.2	−193.5	−193.1
	5.18	1.72	1.64	1.76	−103.0	−194.6	−194.5	−194.6
	5.10	1.72	1.64	1.76	−105.6	−194.6	−194.5	−194.6
2,500	9.38	7.16	6.89	7.45	+ 17.3	− 20.5	− 17.8	− 16.8
	8.61	6.29	6.05	6.53	− 4.9	− 48.9	− 46.5	− 46.0
	7.75	5.29	5.07	5.48	− 29.8	− 81.2	− 80.0	− 79.2
	6.80	4.02	3.85	4.17	− 57.2	−121.5	−120.7	−119.9
	5.76	2.34	2.23	2.42	− 87.0	−174.9	−174.8	−174.1
	5.49	1.74	1.66	1.87	− 94.6	−193.9	−193.8	−191.2
	5.43	1.73	1.65	1.78	− 96.3	−194.2	−194.2	−194.0

TABLE III.—*Continued.*

Final Results.

Pressure.	Thermometer Resistances (Corrected).				Temperatures.			
	Inflow.	No. 1.	No. 2.	No. 3.	Inflow.	No. 1.	No. 2.	No. 3.
Lbs.	Ohms.	Ohms.	Ohms.	Ohms.	Deg.	Deg.	Deg.	Deg.
2,500	5.35	1.72	1.64	1.76	− 98.6	−194.6	−194.5	−194.6
	5.21	1.71	1.63	1.75	−102.4	−194.9	−194.8	−194.9
	5.10	1.71	1.63	1.75	−105.6	−194.9	−194.8	−194.9
3,000	9.49	7.14	6.90	7.45	+ 20.5	− 21.1	− 17.4	− 16.8
	8.63	6.13	5.89	6.36	− 4.3	− 54.0	− 52.0	− 51.4
	7.94	5.33	5.10	5.50	− 24.3	− 79.9	− 79.0	− 78.6
	7.48	4.76	4.56	4.91	− 37.6	− 98.0	− 97.0	− 96.9
	6.55	3.40	3.25	3.51	− 64.4	−141.2	−140.7	−140.3
	5.60	1.76	1.68	1.85	− 91.5	−193.3	−193.1	−191.8
	5.52	1.74	1.65	1.77	− 93.8	−193.9	−194.2	−194.3
	5.47	1.73	1.65	1.77	− 95.2	−194.2	−194.2	−194.3
	5.27	1.73	1.64	1.77	−100.9	−194.2	−194.5	−194.3

opposite effect. The differences should become less at higher temperatures and disappear altogether when the blast has the temperature of the room. They are due on the contrary to the high velocity at which the blast enters the outflow tube through the orifice at the top, and the reading of no. 3 is to be considered the true final temperature, as has been already explained.

When the blast at the mouth of the outflow tube contains liquid air, there is of course no longer any possibility of local differences of temperature within the tube. Doubtless the ratio of liquefied to unliquefied air is greater at the top than at the bottom, on account of the differences of velocity, but the temperature is the same.

If the initial temperature is a suitable one, liquid may exist indeed only at the upper part of the tube. Instances of this are found in the tenth reading for 1,000 lbs., the tenth and eleventh for 1,500 lbs., the seventh for 2,000 lbs., etc., where no. 1 or nos. 1 and 2 record the temperature of liquid air, while no. 3 is higher.

Fig. 4 displays the nature of the curves which are obtained by plotting initial temperatures as abscissas and final temperatures as ordinates.

The curves exhibit certain unmistakable facts.

It is clear that the final temperature falls more rapidly than the initial temperature, instead of less rapidly, as Pictet's formula re-

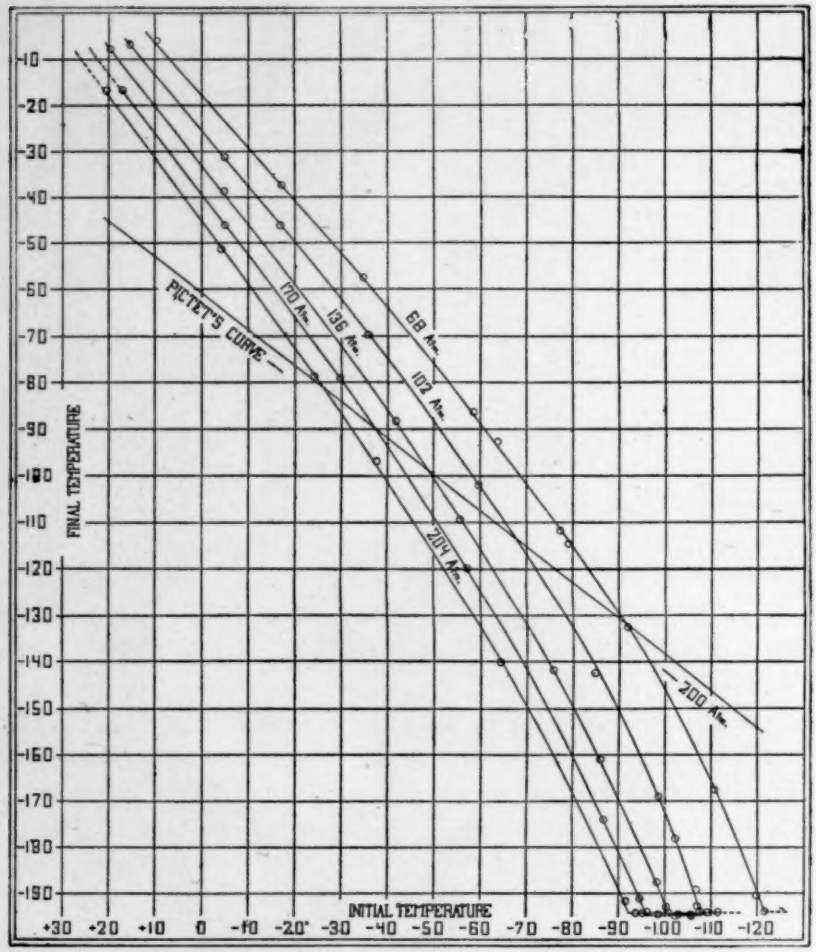

Fig. 4.

quires. Qualitatively, this result is in accord with the view of Linde and Schrötter. For the sake of better comparison, Pictet's curve for 200 atm. is plotted with the rest. For all pressures between 100 atm. and 200 atm., his curves are practically identical, as has been said.

Again, it is clear that at none of these pressures does the air on the high pressure side of the valve need to descend to the critical temperature in order to produce liquid air. At 1,000 lbs. pressure, the initial temperature descends only to — 121°; at 1,500 lbs., to

— 107.5°; at 2,000 lbs., to — 101°; at 2,500 lbs., to — 96.5°; and at 3,000 lbs., to only — 93°. Indeed at 3,000 lbs. liquefaction is attained at the valve from an initial temperature which is forty degrees higher than the critical temperature, and by a cooling effect of approximately one hundred degrees, where the formula of Pictet allows only forty. It is certain therefore that the use of high pressure does not tend to promote liquefaction in the high pressure circuit, as Pictet fears, but just the reverse. The further question whether liquefaction in the high pressure circuit would be deleterious if it did occur, has already been answered in the negative.[1]

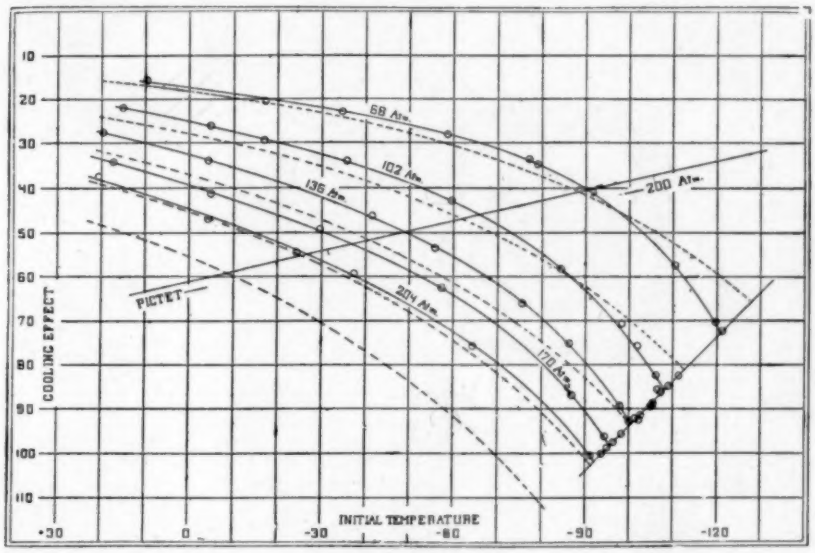

Fig. 5.

Thus the view of Linde is qualitatively vindicated. In order to exhibit the quantitative relations between our results and those called for by the views of Linde and Pictet, it will be more convenient to plot initial temperatures against the cooling effect. This is done in Fig. 5, with initial temperatures and cooling effect as abscissas and ordinates respectively.

In the figure the results obtained by us are represented by the circular plots and the continuous line curves are drawn through them

[1] Bradley and Fenwick, Journal of Physical Chemistry, *10*, 275–289, 1906. Cottrell, ibid., 264–274.

as smoothly as possible. These curves terminate at the right in a rectilinear representing liquefaction. The dotted curves are calculated from the formula of Joule-Kelvin.

The curve for Pictet's formula is seen still more clearly than before to resemble the experimental ones in no respect whatsoever. Indeed, it is difficult to see how that formula could have been based upon experimental data at all.

On the other hand, the Joule-Kelvin curves show a pronounced general similarity to our own, though they differ markedly in certain details. Thus, every one of them, at least for the greater portion of its length, lies lower than the corresponding experimental ones, and the difference between corresponding curves becomes rapidly greater as the pressure increases. At 68 atm., the difference is about one degree for an initial temperature of — 20°, while at 204 atm. it is ten. At 68 atm., it is two and one half degrees for an initial temperature of — 80, while at 204 atm., it is twenty-three.

On the contrary, for low pressures and *low initial or final temperatures*, the cooling effect according to the Joule-Kelvin formula is considerably *less* than that which we have observed. At the point of liquefaction it is twelve and one half degress less for 68 atm., and nine degrees less for 102 atm. For 136 atm., the two curves are practically coincident at the point of liquefaction.

It is evident therefore that the situation is much more complicated at high pressures and at low temperatures than is represented in the Joule-Kelvin formula, which was derived from experimental results at moderate temperatures and pressures.

Before entering upon a discussion of this question, certain other matters must be considered.

It has already been mentioned that expanded air, close to the valve, is colder than that farther away, even under satisfactory conditions of insulation. This phenomenon is explained as due to the greater kinetic energy of the air so long as it retains any portion of the abnormal velocity which it acquires in passing through the minute aperture of the valve. Thus Travers:[1] "The increase in the kinetic energy of the issuing gas necessitates an absorption of heat, so that there would be a fall of temperature — implying a

[1] Study of Gases, p. 190.

conversion of molecular kinetic energy into translational energy of the mass of the gas. This fall of temperature, which may be termed *velocity cooling*, would disappear at a short distance from the plug, the velocity of the stream of gas being reduced by friction within the walls of the tube or with the gas in the vessel into which it flows, resulting in the formation of eddies ; the kinetic energy of the stream of gas would thus be reduced to its original value. The effective cooling of the gas is the result of internal work only, though the velocity cooling which takes place close to the plug or valve, through which the gas is escaping, may result in a fall of temperature greater than could be accounted for by the Joule-Thomson effect ; the velocity cooling would, however, be confined to a very limited region."

In order experimentally to eliminate velocity cooling, so as to study the Joule-Kelvin effect alone, it would be necessary to provide such mechanical conditions as should give the air after expansion the same velocity which it had before reaching the valve. This is a difficult, if not wholly impossible task. If the question was simply one of relative initial and final pressures, equal velocity before and after expansion could easily be secured by giving the high pressure pipe and the outflow tube sectional areas in the clear which should be to each other inversely as the pressures — that is, in practice, by using different outflow tubes having different sectional areas for each change in the pressure ratio. But complication enters from the fact that the Joule-Kelvin cooling effect increases inversely as the square of the initial temperature, so that for every initial temperature there is a different volume ratio between the compressed and the expanded air, and therefore a change in the velocity ratio also. Equal velocities before and behind the valve could only be secured in practice by changing the outflow tube, not only for every change in the pressure ratio, but for every change in the temperature ratio as well.

However, it was hoped that the effect of velocity cooling might be eliminated by calculation, provided the total cooling effect was determined through the use of a set of outflow tubes of sufficiently diverse diameter. Our original plan contemplated the determination of a complete set of readings like that of Table III. for each one of

the tubes in the set, and we were not a little surprised at the discovery that such a procedure was quite unnecessary, as will now be shown.

TABLE IV.

Pressure.	Temperatures. Tube *A*—39.2 sq. mm.				Final Temp. Tube *B*.	Differences.	Average Difference.
	Inflow.	No. 1.	No. 2.	No. 3.			
Lbs.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.
1,000	+ 12.4	− 2.3	− 2.1	− 2.8	− 2.5	−0.3	
	− 8.4	− 27.2	− 27.0	− 26.9	− 27.0	+0.1	
	− 51.4	− 77.6	− 77.3	− 77.4	− 77.7	+0.3	+0.14
	− 72.2	−104.4	−104.0	−104.3	−104.6	+0.3	
	−101.3	−149.1	−149.0	−149.0	−149.3	+0.3	
1,500	+ 8.9	− 14.2	− 14.3	− 14.5	− 14.6	+0.1	
	− 8.4	− 37.0	− 35.5	− 36.1	− 35.7	−0.4	
	− 38.5	− 74.1	− 73.5	− 73.6	− 73.4	−0.2	
	− 65.9	−112.0	−112.1	−111.8	−111.4	−0.4	−0.30
	− 81.4	−139.0	−138.7	−138.4	−137.0	−1.4	
	− 96.5	−166.0	−165.5	−165.1	−165.0	−0.1	
	−104.4	−185.7	−183.2	−183.1	−183.5	+0.4	
2,000	+ 10.7	− 19.3	− 19.4	− 19.4	− 19.0	−0.4	
	− 22.2	− 62.8	− 62.6	− 62.5	− 62.0	−0.5	
	− 47.9	− 97.7	− 98.0	− 97.8	− 97.1	−0.7	−0.70
	− 74.2	−139.3	−139.0	−139.0	−138.6	−0.4	
	− 92.6	−177.4	−176.5	−176.3	−174.8	−1.5	
2,500	+ 12.1	− 25.3	− 23.9	− 24.1	− 23.7	−0.4	
	− 25.4	− 74.3	− 74.1	− 74.2	− 74.0	−0.2	
	− 53.7	−114.5	−114.7	−114.9	−114.6	−0.3	−0.50
	− 74.2	−153.3	−152.3	−152.1	−149.3	−2.8	
	− 79.7	−162.1	−161.7	−161.7	−159.8	−1.9	
	− 84.2	−169.8	−169.4	−169.1	−168.8	−0.3	
3,000	− 13.0	− 29.1	− 27.7	− 27.9	− 27.7	−0.2	
	− 14.8	− 65.0	− 64.3	− 65.0	− 65.5	+0.5	+0.08
	− 52.3	−121.2	−120.7	−120.5	−120.3	−0.2	
	− 83.1	−175.2	−174.1	−173.5	−173.7	+0.2	

Table IV. gives some sample temperature readings during the use of our smallest outflow tube. This tube had an available sectional area, between its inner wall and the outer wall of the thermometer pocket, of 39.24 sq. mm. As before, the records of all three of the thermometers were taken. For comparison's sake, interpolated values from Table III. are given for thermometer no. 3. Table III. was obtained by the use of an outflow tube (*B*) of 669.5 sq. mm. net sectional area.

Thus the use of the smallest outflow tube, though it increases the velocity of the expanded air seventeen fold, increases the apparent cooling effect by only four tenths of a degree.

It may be noted parenthetically that the difference of the readings of themometers no. 1 and no. 2 for high initial temperature is very much less in Table IV., during the use of the smallest outflow tube, than in Table III. The reason is a simple one. When the thermometer pocket was attached to this tube in the manner already described, it was found that its flange and straps practically closed the mouth of the latter. In order to provide room for the escape

TABLE V.

Pressure.	Temperatures. Tube *C*—1,552 sq. mm.				Final Temp. Tube *B*.	Differences.	Average Difference.
	Inflow.	No. 1.	No. 2.	No. 3.			
Lbs.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.
1,000	− 39.6	− 66.3	− 63.9	− 63.1	− 63.5	+0.4	+0.1
	−113.7	−177.1	−175.8	−175.6	−175.4	−0.2	
1,500	− 38.7	− 76.3	− 74.1	− 73.9	− 73.7	−0.2	+0.1
	−105.8	−191.7	−188.4	−187.4	−187.8	+0.4	
2,000	− 37.6	− 83.4	− 83.1	− 82.3	− 82.3	0	−0.35
	− 89.3	−169.5	−168.8	−168.5	−167.8	−0.7	
2,500	− 36.1	− 90.4	− 89.3	− 88.5	− 88.7	+0.2	−0.6
	− 81.4	−165.6	−164.8	−164.5	−163.0	−1.5	
3,000	− 83.4		−175.1	−174.1	−174.7	+0.6	+0.6

of the expanded air, suitable washers were therefore used between the flange of the outflow tube and the straps of the thermometer pocket. But this brought the upper end of the pocket correspondingly farther away from the region of excessive velocity, and abnormal cooling effect, in the tip of the outflow tube.

The next table contains readings taken during the use of the largest outflow tube of the set. This tube had a net sectional area of 1,552 sq. mm., giving a velocity less than one fortieth that of the smallest tube, and about one half that of tube *B* by which Table III. was obtained. As only small differences were now expected, very few readings were made.

The result is an apparent average *increase* in the cooling effect of one tenth of a degree. With the widest outflow tube the cooling

effect should be least. However, all of the differences, both in Table IV. and in Table V., are so small that only a very large increase indeed in the number of the observations would enable them to be distinguished with certainty from observational errors.

Thus it is evident that under any ordinary circumstances, velocity cooling forms a negligible factor in the total cooling effect of nozzle expansion, except indeed very close to the valve.

Naturally this conclusion simplifies very greatly the task of interpreting the results in Table III. However, to make assurance doubly sure, we tried the effect of enlarging four fold the free sectional area of the high pressure tube in front of the valve, that of the inflow thermometer pocket, and that of the valve seat. The outflow tube "*B*" was used as in Table III. Following are the results:

TABLE VI.

Pressure.	Temperatures. Enlarged Supply Pipe.				Final Temp. Table III.	Differences.	Average Difference.
	Inflow.	No. 1.	No. 2.	No. 3.			
Lbs.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.	Deg.
1,000	−42.2	− 69.9	− 67.3	− 66.3	− 66.9	+0.6	
	−86.5	−125.6	−124.0	−123.6	−125.1	+1.5	
1,500	−35.0	− 71.8	− 69.4	− 68.5	− 68.8	+0.3	
	−81.4	−137.0	−135.4	−135.3	−136.7	+1.4	+0.8
2,000	−36.1	− 82.7	− 81.0	− 80.2	− 80.4	+0.2	
	−75.1	−141.2	−140.0	−139.5	−140.2	+0.7	
2,500	−35.3	− 89.2	− 87.7	− 87.0	− 87.3	+0.3	
	−79.4	−158.6	−157.8	−157.3	−158.6	+1.3	

Several things may be noted in this table. First, the differences are all of the same sign. Enlargement of the supply tube has had a decided effect, apparently. Second, the sign is not the one which was to have been expected. The cooling effect is less, instead of greater. Enlarging the supply tube, by increasing the velocity ratio between the expanded air and that in the high pressure region, should have the same kind of effect as the use of a small outflow tube, as in Table IV. Third, the differences are in every case several times greater for low initial temperatures than for higher ones. Fourth, apparently, the amount of pressure employed has very little, if anything, to do with any of the changes exhibited in this

table. However, the differences are not great enough numerically to introduce any essential change in the conclusions derived from our main results. They are scarcely greater than the experimental errors.

It is well known that for various reasons the output of a compressor changes somewhat from day to day, and even from hour to hour during a single run. When these changes occurred during a single run, they proved very annoying, for they not only necessitated such a manipulation of the valve as would keep the initial pressure constant, but often occasioned considerable delay in the temperature readings, until a new equilibrium could become established in the interchanger. Still, when once the equilibrium had become established, we could never observe that the cooling effect had become abnormal.

However, it seemed desirable to test experimentally the effect of considerable variations in the amount of air forced through the valve. This was done in two ways: — during the preliminary stage of the work, by changing the speed of the compressor; later, in the much more convenient way of throttling the intake of the same. By the latter method especially the amount of air delivered was easily changed within a few minutes from the normal rate of twenty cubic feet to about ten per minute, and then back again. Although considerable time was spent in the attempt, we could never detect any essential change in the results. Such changes had one very noticeable effect, which threw a side light upon the efficiency of the hair felt insulation about the interchanger. For example, in one sample experiment, taken almost at random, the full amount of air was being pumped, and was precooled as already explained, by ammonia. The pressure was 2,000 lbs., and very little of the interchanger was exposed to the exhaust. The initial temperature was $-39.3°$, and the final temperature was perfectly steady at $-85.4°$. At once the compressor output was cut down one half, and the expansion valve adjusted to correspond. The air entering the interchanger now took twice as long as before to reach the valve and so was exposed twice as long to the inflow of heat through the insulation. The result was a gradual rise of the initial temperature to $-30.6°$, and of the final temperature to $-72.9°$. Then the intake of the compressor was thrown open and the full amount of

air was again delivered. The initial temperature fell steadily to $-38.7°$, and the final temperature to $-84.8°$. All three of these final temperatures are normal for the corresponding initial temperatures, as one may see by interpolating for the latter in Figs. 4 or 5.

As the valve was originally constructed, the face of the stem, as well as that of the valve seat, stood at right angles to the direction of the flow of the compressed air. Thus, at the moment of expansion, the air turned abruptly at right angles in order to reach the little cavity around the stem. Although it was not clear how this arrangement could affect the results, the valve was changed for the sake of testing the matter. The stem was made conical in the positive sense, and the seat, in the negative. Still, the cooling effect was the same, within the limits of error.

The same held true after a further modification, whereby the sectional area of the narrow passage leading downward from the valve cavity to the top of the outflow tube was increased sixteen fold.

In short, it is apparent that within the limits of error, the only factors which determine the cooling effect when air expands from a high pressure to one atmosphere are the pressure difference and the initial temperature. This brings us back to a discussion of Table III. and the curves of Fig. 5.

At first, the approximate parallelism between these curves and those calculated from the Joule-Kelvin formula led to the hope that, by a simple change in the constants, that formula might continue to serve. In this we were disappointed. It is true that by substituting for the expression $0.276\ (p_2 - p_1)$, $0.276\ (p_2 - p_1) - 0.017\ (p_2 - p_1)^2$, curves are obtained which are practically coincident with the experimental ones over about three fourths of their length. The following table shows this. The "observed" values are read from the smoothed curves of Fig. 5.

It will be noticed that the differences are within the limits of error down to an initial temperature of $-80°$, for 68 atm. and for 170 atm.; to $-60°$, for 102 atm.; and to $-50°$, for 136 atm. Beyond these limits they become rapidly larger, and with the minus sign. That is, the modified Joule-Kelvin curves diverge from, and lie above those which are derived from observation, and represent thereafter a lesser cooling effect.

TABLE VII.

Modified Joule-Kelvin Formula.

Initial Temperature.	"p_2-p_1"								
	68.03 Atm.			102.04 Atm.			136.05 Atm.		
	"d" Calc.	"d" Obs.	Diff.	"d" Calc.	"d" Obs.	Diff.	"d" Calc.	"d" Obs.	Diff.
0	17.6	17.1	+ .5	25.6	25.0	+ .6	32.9	32.6	+ .3
− 10	19.0	18.7	+ .3	27.6	27.4	+ .2	35.5	35.6	− .1
− 20	20.5	20.3	+ .2	29.8	30.0	− .2	38.3	38.7	− .4
− 30	22.2	21.9	+ .3	32.3	32.7	− .4	41.6	42.1	− .5
− 40	24.2	23.8	+ .4	35.1	35.7	− .6	45.2	46.0	− .8
− 50	26.4	25.8	+ .6	38.3	39.0	− .7	49.4	50.4	− 1.0
− 60	29.0	28.2	+ .8	42.0	43.0	− 1.0	54.1	55.5	− 1.4
− 70	31.9	31.6	+ .3	46.3	48.3	− 2.0	59.6	61.8	− 2.2
− 80	35.3	35.4	− .1	51.2	54.9	− 3.7	65.9	69.5	− 3.6
− 90	39.2	40.2	−1.0	56.9	63.4	− 6.5	73.3	79.5	− 6.2
−100	43.9	47.4	−3.5	63.7	74.3	−10.6	82.0	92.8	−10.8
−110	49.4	57.2	−7.8						
	170.07 Atm.			204.08 Atm.					
0	39.7	39.4	+ .3	45.9	44.6	+1.3			
− 10	42.8	42.6	+ .2	49.5	48.2	+1.3			
− 20	46.2	46.0	+ .2	53.5	52.1	+1.4			
− 30	50.1	49.7	+ .4	58.0	56.4	+1.6			
− 40	54.5	54.0	+ .5	63.0	61.1	+1.9			
− 50	59.5	58.7	+ .8	68.8	66.4	+2.4			
− 60	65.2	64.2	+1.0	75.4	72.5	+2.9			
− 70	71.8	71.0	+ .8	83.0	79.5	+3.5			
− 80	79.4	79.6	− .2	91.9	88.2	+3.7			
− 90	88.3	91.6	−3.3	102.2	99.2	+3.0			

The differences for 204 atm. are all rather large, and they become larger as the initial temperature falls. Moreover, they all have the plus sign, meaning that the calculated cooling effect throughout is greater than it should be.

It became quickly evident therefore that in all probability time would be saved in the end by deriving a new formula directly from the experimental results.

Indeed, two such formulas will be given. They will be called formulas *A* and *B* respectively. Each of them fits the facts within the limits of error. Unfortunately, both of them are rather complicated.

For the suggestion which led to Formula *A*, we are indebted to

Mr. T. E. McKinney, Ph.D., who was at the time associate professor of mathematics in this University. It was suggested, namely, that the general formula

$$d = a_0 + \frac{a_1}{T - a_2}$$

could doubtless be made to represent the cooling effect observed under each one of the five pressure differences, by assigning five sets of values to a_0, a_1 and a_2 (T being the initial temperature on the absolute scale) and that then, without too great complication, the five values for each of these constants might prove capable of interpretation as functions of the pressure difference, P. So far at least as a_0 and a_1 are concerned, the expectation proved well founded. The case of a_2 was more complicated. Formula A follows:

$$d = 23.9 - \frac{7,801.5}{379.65 - P} + \frac{\dfrac{6,833,400}{449.66 - P} - 14,905}{T - 84.8 - .54516P + 9.4648 \times 10^{-4}P^2 + 2.3973 \times 10^{-5}P^3 - 7.0977 \times 10^{-8}P^4}.$$

Table VIII. gives a comparison of the observed cooling effect with that calculated by Formula A.

Fig. 6 illustrates the cooling effect as calculated by means of Formula A. As before, the circular plots represent the experimental results. As will be seen, the curves fit rather better for initial temperatures below $-40°$, or thereabouts, than for temperatures above that point.

For the derivation of *Formula B*, we are under obligations to Mr. B. H. Camp, M.A., of the mathematical department. P, as before, is the pressure difference in atmospheres, and d is the cooling effect, but t is the initial temperature in degrees of the Centigrade scale.

$$d = 0.2754P - 2.744 \times 10^{-4}P^2 - (2.617 \times 10^{-3}P - 4.991 \times 10^{-6}P^2)t - (4.175 \times 10^{-7}P - 3.86 \times 10^{-5})t^3 - (4.175 \times 10^{-9}P + \frac{(163.3 - P)^2}{4.649 \times 10^{10}} - 7.341 \times 10^{-7})t^4.$$

TABLE VIII.

Formula A.

P (Atm.)	Cooling Effect (d).			Av. $d_c - d_o$
	d_c	d_o	$d_c - d_o$	
68.03	16.2	15.8	+ .4	
	19.4	20.3	− .9	
	22.3	23.0	− .7	
	27.7	27.7	0	
	29.2	28.7	+ .5	
	34.1	34.4	− .3	−.2
	34.8	35.5	− .7	
	41.3	41.1	+ .2	
	56.8	57.0	− .2	
	69.6	70.6	−1.0	
	72.5	72.3	+ .2	
102.04	22.7	22.0	+ .7	
	26.2	26.2	0	
	28.7	29.2	− .5	
	33.7	33.9	− .2	
	42.7	42.1	+ .6	
	58.1	57.7	+ .4	+.1
	72.2	70.3	+1.9	
	77.0	75.7	+1.3	
	83.0	82.6	+ .4	
	83.8	85.7	−1.9	
	84.7	86.4	−1.7	
136.05	28.4	27.3	+1.1	
	33.8	34.1	− .3	
	46.1	46.3	− .2	
	53.0	53.6	− .6	+.1
	66.1	66.2	− .1	
	75.6	75.2	+ .4	
	89.9	89.6	+ .3	
	92.8	92.9	− .1	
170.07	34.4	34.1	+ .3	
	40.4	41.1	− .7	
	49.2	49.4	− .2	
	62.9	62.7	+ .2	−.2
	86.9	87.1	− .2	
	95.5	96.6	−1.1	
	97.7	97.7	0	
204.08	38.6	37.3	+1.3	
	46.2	47.1	− .9	
	53.9	54.3	− .4	+.3
	60.1	59.3	+ .8	
	76.3	75.9	+ .4	
	101.1	100.3	+ .8	

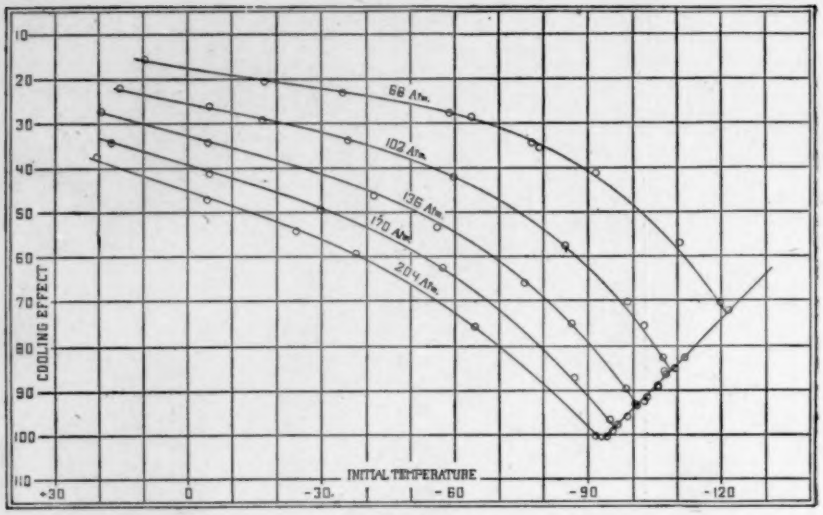

Fig. 6.

The cooling effect as calculated by Formula *B* is compared with the observed cooling effect in Table IX. and in Fig. 7.

As Formula *A* accords a little better with the observed cooling effect for lower initial temperatures, so Formula *B* accords rather

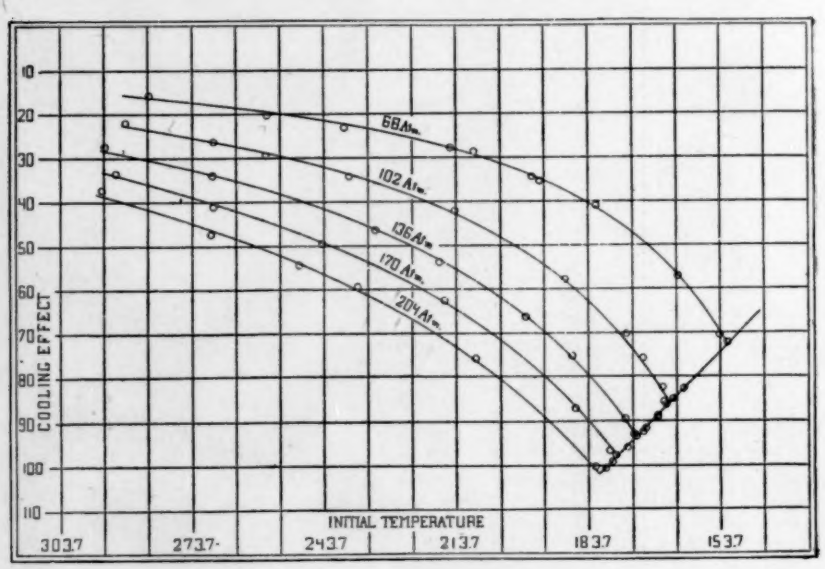

Fig. 7.

TABLE IX.

Formula B.

P (Atm.)	Cooling Effect (d).			
	d_c	d_o	$d_c - d_o$	Av. $d_c - d_o$
68.03	16.0	15.8	+ .2	
	20.1	20.3	− .2	
	22.8	23.0	− .2	
	27.6	27.7	− .1	
	29.0	28.7	+ .3	
	33.9	34.4	− .5	+.3
	34.7	35.5	− .8	
	42.0	41.1	+ .9	
	59.0	57.0	+2.0	
	71.2	70.6	+ .6	
	73.8	72.3	+1.5	
102.04	22.2	22.0	+ .2	
	26.5	26.2	+ .3	
	29.1	29.2	− .1	
	33.7	33.9	− .2	
	42.1	42.1	.0	
	57.9	57.7	+ .2	−.2
	72.2	70.3	+1.9	
	76.7	75.7	+1.0	
	82.7	82.6	+ .1	
	83.2	85.7	−2.5	
	83.9	86.4	−2.5	
136.05	27.4	27.3	+ .1	
	33.9	34.1	− .2	
	45.5	46.3	− .8	
	52.2	53.6	−1.4	−.3
	65.6	66.2	− .6	
	75.4	75.2	+ .2	
	89.8	89.6	+ .2	
	92.6	92.9	− .3	
170.07	33.9	34.1	− .2	
	40.7	41.1	− .4	
	49.1	49.4	− .3	
	62.8	62.7	+ .1	+.3
	88.1	87.1	+1.0	
	97.0	96.6	+ .4	
	99.1	97.7	+1.4	
204.08	38.1	37.3	+ .8	
	46.6	47.1	− .5	
	53.7	54.3	− .6	−.1
	59.6	59.3	+ .3	
	76.0	75.9	+ .1	
	99.9	100.3	− .4	

better with the cooling effect for the higher initial temperatures. Indeed, it was Formula *B* and its curves which first called attention to the fact that the observed cooling effect from 0° C. upward almost involves an inflexion of the curvature which prevails below that point. At that time, unfortunately, it was too late to enter upon the matter again experimentally. It is clear, however, that such an extension of the present inquiry is much to be desired.

Since the experimental part of this paper was completed, much interest has been taken regarding the nature and location of the so-called inversion point of air and other gases, that is, the temperature, or temperatures, at which the cooling effect is zero. Particular reference may be made to the experimental work of Olszewski,[1] and the calculations of Dickson,[2] based on van der Waals' equation of state.

In 1898 Witkowski showed that the inversion point must be a function of the pressure. This was confirmed by Porter[3] and by Dickson,[2] on theoretical grounds, as well as by the experimental results of Olszewski. However, the relation of the inversion point to the pressure is a direct one according to Olzewski, in harmony with the deductions of Porter, while according to Dickson it should be an inverse one.

Again, Olszewski finds the inversion temperatures to lie between 198°–259° Centigrade for pressures ranging from 40 to 160 atm., while, according to Dickson's calculations, they should lie between 607.3° and 555°. Porter's calculations are for hydrogen only.

It is to be noted, as Dickson points out, that these discrepancies may be accounted for, if it may be assumed that there is some fundamental difference between expansion through a nozzle and expansion through a porous plug.

Under the circumstances, it may not be without interest to compare Formulas *A* and *B* as given above, by setting $d = 0$ in each, for the five pressures used in this work. When this is done, Formula *A* gives the following results, in Centigrade temperatures.

68.03 atm.	102.04 atm.	136.05 atm.	170.07 atm.	204.08 atm.
2,494°	971°	679°	534°	431°

[1] Philosophical Magazine (6), *13*, 722–4, 1907.
[2] Idem (6), *15*, 126–46, 1908.
[3] Philosophical Magazine (6), *11*, 554–68, 1906.

The method of expansion used in these experiments and in Olszewski's work is probably the same. As the values just given differ greatly in magnitude from those found by Olszewski and as the relation between the calculated inversion temperature and the pressure is an inverse one, it is clear that however closely Formula *A* may correspond to the experimental data from which it was derived, it would not be a safe one to use for high initial temperatures. Indeed, it is our conviction that the cooling effect obtained by the use of a nozzle is a very complicated matter. For almost any narrow range of data, some comparatively simple formula may doubtless be derived which will fit passably well. The hope that any simple formula will be found to represent data of wide range, either of temperature or pressure, is probably futile. This matter will be considered again at the close.

As has been said, Formula *B* corresponds rather better than Formula *A* to the experimental data at the higher initial temperatures. It might be expected therefore that it would lead to a closer approximation to the inversion temperatures. And numerically speaking, this is true for the two highest pressures. Thus for 204.08 atm., the inversion temperature would be 71.8°, and for 170.07 atm. it is 79° Centigrade. The curves for the other three pressures show no point at all where the cooling effect is zero, although that for 136.05 atm. comes within half a degree of doing so, before it turns again downward. It will be noticed moreover that the two inversion temperatures which are given for the higher pressures, bear an inverse ratio to the pressures, as in the case of Formula *A*.

In another connection[1] favorable use has already been made of the theory of the gaseous and liquid states which has been advanced and vigorously defended by J. Traube.[2] There seems good reason to believe that this theory is capable of explaining satisfactorily the phenomena connected with the Joule-Kelvin effect and the inversion temperature. Although the data at hand at present are doubtless much too meager to warrant anything more than tentative, we venture the following suggestions.

[1] Bradley, Brown and Hale, PHYS. REV., *27*, 104, 1908.

[2] Zeitschrift für anorganische Chemie, *37*, 225, 1903; *38*, 399, 1904.

A perfect gas should become warmer on passing through a throttling valve or nozzle, on account of the friction encountered. In making this statement, no regard is paid to changes in kinetic energy during the passage of the valve and immediately afterward, for, if the initial and final velocities are equal, these will compensate one another. Instead of speaking of a gas whose temperature is raised under these circumstances as "ultra perfect," as has somewhat commonly been the practice, particularly in the case of hydrogen, it should rather be considered as more or less approximate to, but still less than, "perfect."

Under any circumstances attainable in practice, a gas is to be thought of as containing in solution, or admixed, some characteristic proportion of "liquidons," a proportion which will depend directly on the pressure and inversely on the temperature. In order to convert these liquidons into true gas molecules (gasons), heat is required.

When a gas expands from a higher pressure to a lower one, by passing through a nozzle, the initial proportion of liquidons will decrease to that which is proper for the new pressure, and an absorption of heat will occur. If the heat thus called for is less than that developed by friction, the net result in the gas as a whole will still be a rise in temperature. On the other hand, when the evaporation of liquidons is copious enough to call for more heat than is produced by friction, a net cooling effect will be obtained. The total cooling effect, and therefore the net cooling effect, if any, will vary directly as the initial pressure, and inversely as the initial temperature and the final pressure.

Probably the heat of friction depends on a considerable number of factors, referable in part to the nature and condition of the gas itself and in part to the materials, condition and structure of the valve or nozzle.

The proportion of liquidons present in the gas at low pressures will not be large unless the temperature becomes greatly lowered. The real cooling effect will therefore not be large except for low initial temperatures. But in proportion as the initial temperature approaches the critical temperature the proportion of liquidons, and therefore the cooling effect, will increase more and more rapidly,

until the rate of increase becomes very great indeed. This appears to be the explanation of the peculiarities of the curve for 68 atm., in Figs. 5, 6 and 7.

At comparatively high pressures, on the other hand, the proportion of liquidons will be greater at all times, and so, by consequence, will the cooling effect be. But as the cooling effect is so much greater, liquefaction will be reached while the initial temperature is much further from the critical temperature. Therefore the region of rapid increase in the cooling effect will be greatly restricted or even eliminated. The high pressure curve will terminate in the rectilinear of liquefaction before any sharp increase in its curvature is possible. This condition of things is illustrated in the curve for 204 atm., which is much lower, much shorter, and of much less pronounced curvature at the lower end than any of the others. This curve indeed is to be thought of as "corresponding" only to those portions of the other curves, which lie directly above it — its section of sharp curvature at the right having been eliminated by the earlier occurrence of liquefaction.

From this view-point the inversion temperature would be the temperature at which the cooling effect due to the evaporating liquidons exactly counterbalances the heat due to friction. Naturally this temperature would be higher for higher pressures, as Olszewski has shown, because of the greater proportion of liquidons which are then present.

Summary.

1. The cooling effect produced by the nozzle expansion of air has been studied experimentally for initial temperatures ranging from + 20° to — 120°, and for pressures from 68 atm. to 204 atm.

2. The cooling effect is a direct function of the initial pressure and an inverse function of the initial temperature. This result is qualitatively in harmony with the formula commonly used to express the results of the Joule-Kelvin effect, as applied in particular to the liquefaction of air by Linde, but is diametrically opposed to the formula by which Pictet expresses his view of nozzle expansion.

3. For moderate initial temperatures, the cooling effect is less than that called for by the Joule-Kelvin formula, and the disparity becomes increasingly greater as the pressure increases.

4. For low initial temperatures, the cooling effect becomes rapidly greater than that which the formula indicates, provided the pressure is not too great. At the higher pressures the experimental curves tend to become more nearly parallel to those calculated from the formula.

5. Within the limits of error the cooling effect is not modified by changes in the kinetic energy (velocity cooling) whose ratio is as great as 40 : 1 ; by the form given to the surfaces of the valve stem and seat ; nor by considerable changes in the volume of air which is made to pass the valve.

6. Two formulas, A and B, are derived from the experimental data. The differences between the observed cooling effect and that calculated by these formulas are only infrequently greater than one degree, and average two or three tenths of a degree.

7. So far as these formulas lend themselves to the calculation of the inversion temperatures of air, the latter are inverse functions of the pressure. But the extrapolation is too extreme to be of significance.

8. Certain suggestions are made looking toward an explanation of the Joule-Kelvin effect.

It is intended to undertake at once an extension of the range of these experiments, to include much higher temperatures. The interest which attaches at present to the subject of inversion temperature, as well as certain anomalies observed in connection with the higher of the temperatures already employed, seem to make this highly desirable.

Wesleyan University,
Middletown, Conn.,
February 10, 1909.

THE EFFECT OF TEMPERATURE VARIATIONS ON THE LUMINOUS DISCHARGE IN GASES FOR LOW PRESSURES.

By R. F. Earhart.

IN 1903 Carr[1] made a series of observations on the potential difference required to cause a discharge of electricity between parallel plates, for distances varying from 1 mm. to 10 mm., and for different pressures.

It is well known that for a particular distance a pressure exists at which a minimum potential difference will produce a discharge. Either lowering or increasing the pressure will require a higher potential for the ionization of the gas. The pressure corresponding to the minimum potential is called the critical pressure. Carr found the minimum potential required for discharge to be independent of the distance between the plates. The critical pressure, however, varied with the separation of the plates. The ionization in this case is essentially ionization by collision. The writer has for some time been interested in the effect which temperature would have on the ionization of a gas when the ionization was produced by collision.

I, therefore, determined to repeat Carr's measurements with some slight modifications, subjecting the gas to various temperatures. Before attempting measurements at high temperatures it seemed desirable to carry out a series of measurements with a rather simple form of apparatus for moderate temperatures, in order to find whether consistent results were to be expected at the higher temperatures where one would reasonably expect the effects to be more pronounced. The apparatus which has been used for variations in temperature from $-78°$ C. to $325°$ is shown in Fig. 1. It consists of two circular aluminium plates 1 cm. in diameter and 5 mm. apart. These were enclosed in a glass bulb approximately 4 cm. in diameter, provided with suitable tubes for exhausting and for the introduction of

[1] Proc. Roy. Soc., LXXI., p. 314.

fresh gas, if desired. This bulb was placed in a furnace and heated electrically. The furnace was constructed of a porous battery jar around which a layer of asbestos paper was wrapped; over this was wound No. 18 nickel wire and this surrounded with loose magnesium packing (*P*) several inches in thickness. A thin layer of magnesium paste was used to surface the packing. This furnace

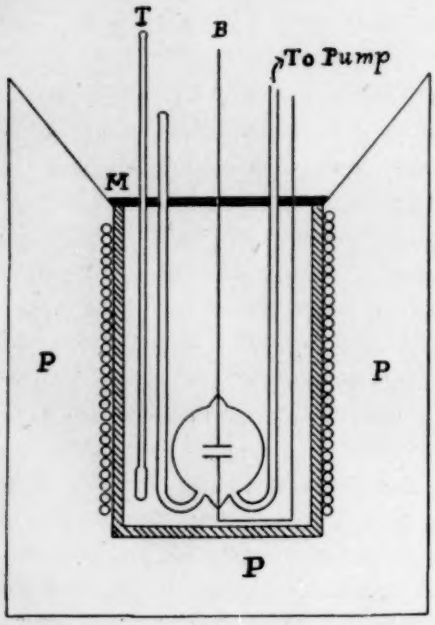

Fig. 1.

was contained in a cylindrical metal box, in order that it might be removed, if desired, and the whole nested in a much larger wooden box containing magnesium packing. The mercury thermometer shown in the figure was used for temperatures below 200° C.; for temperatures above this a Pt resistance thermometer was substituted. After the discharge bulb and thermometer were in place a cover of mica (*M*), in the diagram, closed the furnace, and loose magnesium packing was used to fill in the space above the chamber. For temperatures above that of the room the current in the heating coil was varied until the desired temperature was attained, and after 30 minutes of constancy readings were taken. It is only necessary to know the

approximate temperature and no refinements were attempted. A series of measurements usually occupied three or four hours. Temperatures varying not more than 2 or 3 degrees from the mean were easily secured and considered satisfactory. Pressure measurements were made with the McLeod gauge in the usual manner.

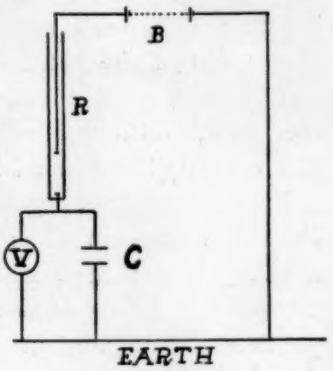

Fig. 2.

The electrical arrangement is shown in Fig. 2. One terminal of a storage battery (B) capable of giving 1,200 volts was connected to earth. The other terminal was connected to one of the plates in the discharge chamber (C) through a liquid resistance of CdI in amyl alcohol (R). The second plate was also connected to earth. A Weston voltmeter (V) together with a suitable multiplier gave the potential difference between the plates in the discharge chamber. The potential required to produce luminosity in the gas was observed.

There is a discharge preceding this, but luminosity marks a sharply defined stage in the ionization of a gas. In general, near the critical pressure, an increase of a single volt will produce a change from no observable luminosity in a dark room, to one which is easily discernible in a lighted room. The behavior of the voltmeter needle during this change from no luminosity to luminosity is a most sensitive detector of the luminous discharge. As the potential is built up by decreasing the resistance in the circuit, the voltmeter needle advances until the luminous discharge occurs and then drops back 40, 50 or even 100 volts, depending on the nature and pressure of the gas. If now the potential be decreased by increasing the resistance in (R), the potential diminishes until the luminous discharge ceases. The voltmeter needle then jumps quickly forward. This motion depends also upon the nature and pressure of the gas. The changes in the potential, which occur as the discharge changes in character from the luminous to non-luminous condition or vice versa, are much less below than above the critical

pressure. This is what one might expect on account of the difference in current density for the two cases. For a time both the luminosity and the behavior of the needle were noted in taking observations, but the connection between the luminosity and the behavior of the needle was so evident to the observer that the direct observation of the luminosity was dispensed with for the higher temperatures. This greatly facilitated the ease of observations. In the tables, which follow, both the potential required to produce luminosity and the potential required to maintain are given.

In an article appearing in the Philosophical Magazine,[1] Mr. J. H. Brown describes an experiment on the current produced after a discharge has been created, and has studied the current density produced for potentials which lie between the potential required to produce the discharge and the potential required to maintain such discharge. He calls attention to the fact that a high resistance in series with the spark gap renders the discharge stable and enables one to secure consistent readings. In so far as the readings tabulated are consistent, I think they were rendered possible by utilizing only a part of the full voltage, which my battery was capable of giving. In order to obtain results at varying temperatures comparable with one another, two factors should be considered, viz., the lag, and the fact that a discharge passing through the gas may raise the temperature of the gas. If the discharge is of long duration, the temperature within the discharge chamber will probably be considerably above that of the vessel in which the chamber is contained, and the thermometer in the outer vessel will not indicate even the approximate temperature of the gas through which the discharge takes place. The generally accepted theory of ionization by collision considers the discharge produced by the action of the field as due to the fact that the strong fields will give great velocity to the free ions existing between the electrodes, and that these ions by their impact on neutral atoms or molecules create a copious supply of fresh ions. Inasmuch as a luminous discharge presupposes the existence of an ionized gas, it seemed legitimate to produce an initial discharge for a brief interval in order to create a supply of ions and after the lapse of a minute or two during which readjustments of

[1] Phil. Mag., Vol. 12, 1906, p. 210.

temperature would take place, to apply a potential, which would produce the luminous condition desired. An illustration of the conditions for producing discharge is inserted.

The apparatus had stood at room temperature for 48 hours, with air as the dielectric, and at a pressure of 3.20 mm. The potential required to produce the initial discharge was 784 volts. The potential was built up of from zero to 784 volts in, perhaps, 5 seconds. The potential was immediately reduced to zero after the luminosity appeared. Two minutes afterward, with the same rate of increasing the potential, luminosity was produced at 502 volts. A repetition two minutes later gave the same result. This was repeated after an interval of seven minutes, when the discharge occurred at 524 volts. Two minutes later the break occurred at 502 volts. I next allowed a seven-minute interval to elapse and raised the potential to 502 volts. After 30 seconds or thereabout, the discharge came. In all cases the potential required to maintain the luminous current was 355 volts. Sets of readings similar to the foregoing were obtained for a number of pressures. The method employed in making the observations was to apply a potential which would cause a discharge, but to maintain this for the briefest possible time, after the lapse of a short interval to build up the potential slowly and to note the occurrence of the discharge, then immediately to lower the potential until the luminous discharge ceased. In this way it was possible to secure consistent readings and to check the potential readings as often as desired. The gases operated upon were air, hydrogen and CO_2. The lowest temperature was secured by using CO_2 snow. The heating chamber was used as a container for the CO_2 snow. The temperature in this case was assumed to be $-78°$ C. Each of the tables which follow are based upon two series of observations. In a single series of observations, usually about 12 points on a pressure potential curve were secured. Another series was taken under similar conditions and 10 or 12 additional points secured. These two series are brought together in a single table.

These are represented graphically in Figs. 3 to 8 inclusive. Fig. 3 is a family of curves representing the values obtained when air was the dielectric. The curve corresponding to 120° is omitted in the graph. The values for this curve agree with one another and

bear the proper relation to the other curves of the family. It was thought, however, that a sixth curve would complicate the figure unduly. The curves are similar in form to those secured by Carr. The results are hardly comparable with his, however. In the present case the discharge might occur at the edges of the plates, whereas in Carr's experiment the discharge was confined to a uniform field. Moreover, Carr measured the potential required to produce the initial discharge. Luminosity occurs, undoubtedly, after the so-called

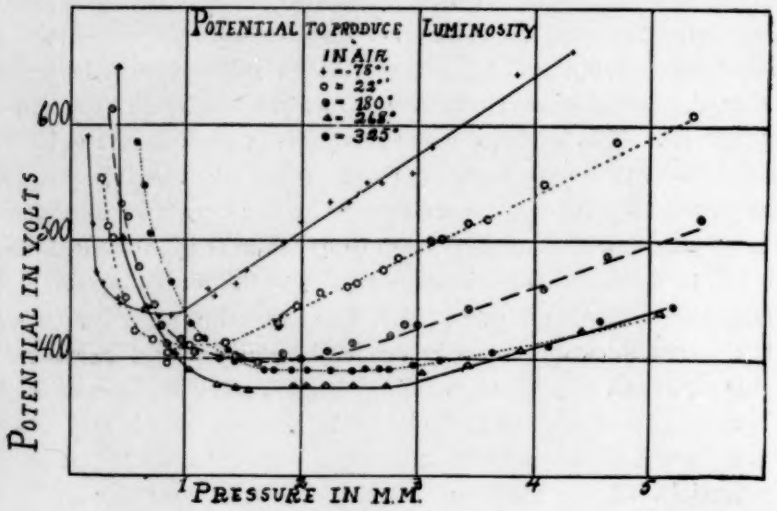

Fig. 3.

dark discharge and marks a more or less advanced stage in the ionizing process. The results do not agree quantitatively with Paschen's Law. Paschen's Law, which applies rather to the initial discharge, states that the potential required for discharge varies with the mass of the gas separating the electrodes. According to Paschen's Law, for pressure greater than the critical pressure, decreasing the pressure will lower the potential required for discharge; for pressures less than the critical pressures diminishing the pressure increases the required potential. In other words, above the critical pressure the potential is lowered as the mass of the gas is decreased, while above the critical pressure decreasing the mass of the gas requires a higher potential.

If we compare similar pressures at different temperatures, then at the higher temperature a smaller mass of gas will exist between the electrodes, and the potential required for discharge be diminished for the higher temperature, provided the pressure is greater than the critical pressure. Again, if the pressure be less than the critical value, raising the temperature will likewise decrease the amount of gas between the electrodes, and this will require higher potentials, as the temperature is increased. For the temperatures from 22° to 268° this holds in a qualitative way, and, with a rough approximation, in a quantitative way. It fails to express the relation between 268° and 325°, even in a qualitative manner. In Fig. 4, the curves which represent the potential required to maintain

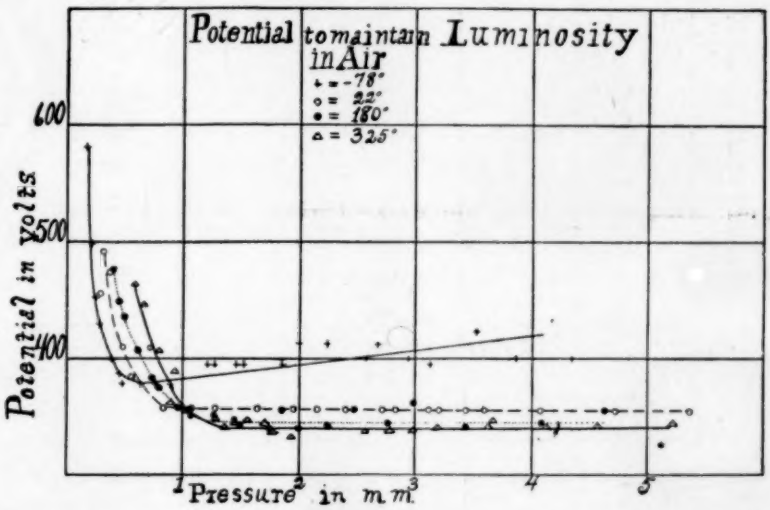

Fig. 4.

luminosity for 120° and 268° are omitted on account of the crowding of the lines.

In the case of air for pressures above the critical pressure the potential required to maintain the luminosity at any temperature is approximately the same for all pressures within the limits of the experiment. Here the curves for the higher temperatures fall below those for the lower temperatures; while below the critical pressure the high temperature curve lies higher than its fellows.

For air at 22° the potential to maintain luminosity was 355 volts. This agrees with the minimum spark potential as measured by Carr, Strutt, Hobbs and others. It is also equal to the cathode fall in potential.

In Figs. 5 and 6 the results secured with hydrogen are repre-

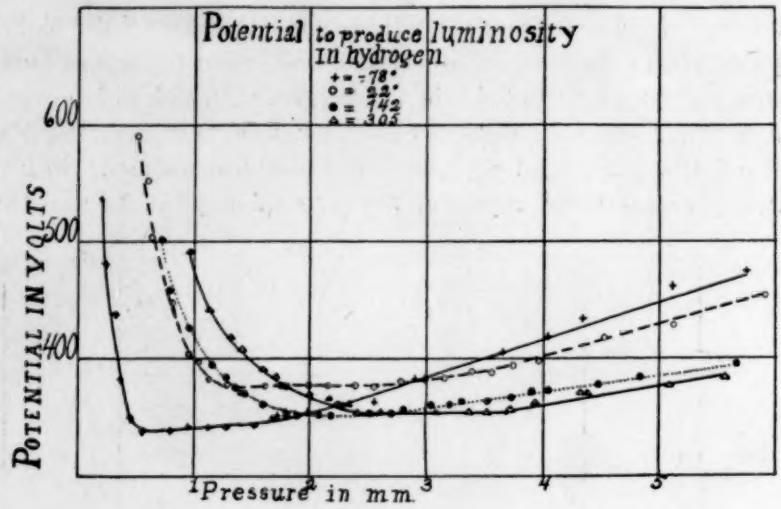

Fig. 5.

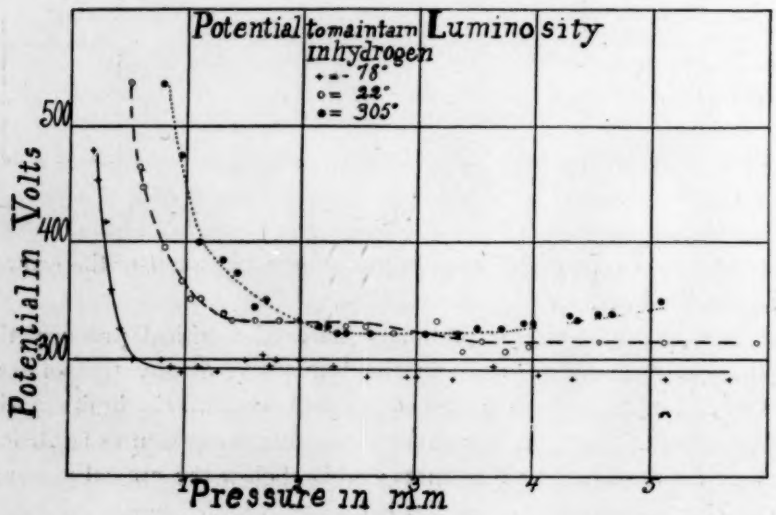

Fig. 6.

sented graphically. The hydrogen was prepared by the action of H_2SO_4 on platinized c.p. zinc. The H was passed through solutions of potassium permanganate and pyrogallic acid, and dried with phosphor pentoxide. Hydrogen of only moderate purity is secured in this manner. I am inclined to believe that the somewhat anomalous results for the potential required to maintain the luminous condition are due to impurities. For $-78°$ the curve is similar to

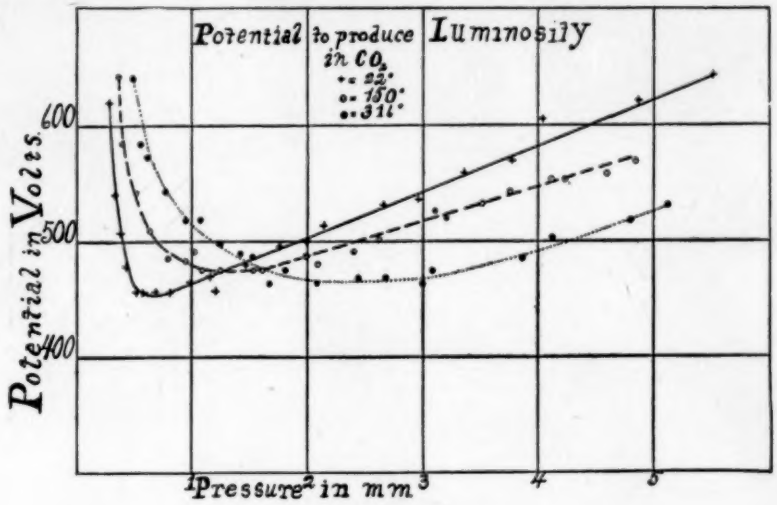

Fig. 7.

the air curve and shows a value of 288 volts. The minimum spark potential for H is given by Carr as 280, and by Strutt as from 301–308 volts.

Many observers have found the phenomenon connected with discharge in hydrogen greatly altered by minute traces of oxygen. After making a series of observations with the moderately good H, I purposely admitted an exceedingly small percentage of air. The potential required to start the discharge was not perceptibly affected; the potential required to maintain discharge was raised considerably.

In case of the carbon dioxide only three temperatures were used. The CO_2 was prepared chemically, using marble and HCl in a Kipp apparatus. The results are indicated in Figs. 7 and 8. After the higher temperature measurements had been made with CO_2 the

lower electrode (cathode) showed evidence of violent bombardment and high temperature. Nothing of this sort occurred with air or hydrogen. After the series of observations at 316° on CO_2, the temperature was inadvertently raised much higher, and in that condition a few discharges produced. An examination of the tube afterward showed no evidence of the tube itself being injured or affected by this higher temperature. The cathode was bent downward and away from the anode and had the appearance of a mushroom.

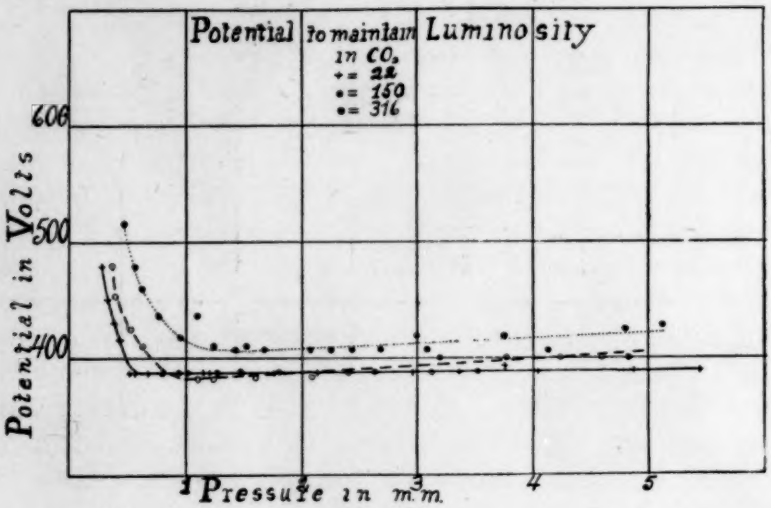

Fig. 8.

No very great accuracy can be claimed for the determination of the critical pressures, especially at the higher temperatures. Indeed, the curves show that for the higher temperatures the region at which the minimum discharge occurs applies to a considerable variation in pressure. For the lowest temperature the location of the critical pressure is determined between rather narrow limits. At 300° C. all of the gases show that a variation in pressure of 2 millimeters may occur without altering the potential required for discharge to any considerable extent. The curves show in general a flattening for this region of minimum potential as the temperature is increased. It seems quite possible that the bend in the curves representing the potential required to maintain discharge will locate the critical pressure more definitely than the discharge curve.

The relation of the curves for air indicates in a general way that there is no particular modification in the mechanism of the discharge until a temperature in the neighborhood of 300° C. is reached. Here the simple relative position of the curves undergoes a change indicating some modifying effect produced near this temperature. The effect of temperature on the potential required to produce the luminous condition is much more apparent than that of the potential required to maintain the luminous condition. In the case of air, increasing the temperature permits a lowering of the potential which will maintain the luminosity. In the case of H and CO_2 the luminous condition is produced at lower potential as the temperature increases, while the potential required to maintain the luminosity is increased. The differences in the latter case for H and CO_2 are extremely small. Since the potential required to maintain the discharge seems to be sensibly affected by traces of foreign gases and the variations are of small magnitude, it is possible that the potential required to maintain the luminosity is not affected through the temperature range used. This would indicate that in the phenomenon connected with Paschen's Law and the effects of pressure and temperature, we are dealing with the mechanism for producing ions. However, it is of equal interest to gather data concerning the conditions where this mechanism ceases to be effective. (Further comment is deferred until more data are available.)

The experiment described is preliminary to one in which it is hoped to study the electrical discharge in the region of the critical pressure and for temperature variations extending up to 800° C. or thereabouts.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY.

ON THE DEFINITION OF AN IDEAL GAS.[1]

BY A. G. WEBSTER AND M. A. ROSANOFF.

THE definition of absolute temperature frequently found in treatises on thermodynamics or on physical chemistry leaves much to be desired. This important quantity is often defined by the equation $pv = RT$, where p and v represent the pressure and specific volume of an ideal gas. We are thus involved in the question, *what is an ideal gas?* To this the answer is often given, one which obeys the two gas laws, that of Boyle and Mariotte, and that of Gay-Lussac and Charles, or combining the two in an equation, $pv = RT$. We are thus led around in a circle to an absurdity. Of course the absolute temperature should not be thus defined, but should be defined from Carnot's principle, as was done by Lord Kelvin. But inasmuch as there are no ideal gases in nature, from which to make thermometers, the verification of how nearly a real gas verifies the definition of an ideal one is a matter of some difficulty. The verification of the law of Boyle is an easy criterion and if to this we add the proper second specification we get a proper definition. This is often done by saying that if the energy of a gas is independent of the specific volume, but depends only on the temperature, the gas is ideal. This may be replaced, as shown below, by the statement that the cohesion of the gas is zero. A third statement is that found, for instance, in a very careful paper by Buckingham, on the thermodynamic scale,[2] in which the correct definition is given, that "the ideal gas is one which follows Boyle's law and in which a free expansion, with no external work, would cause no change in the temperature." This criterion is tested in the Joule-Kelvin porous plug experiment, and the heating or cooling that usually takes place is called the Joule-Kelvin effect.

It is the purpose of this communication to examine in how far

[1] Presented at the meeting of the American Physical Society, October 24, 1908.

[2] Bulletin Bureau of Standards, May, 1907.

these different definitions are identical, and what conclusions can be drawn from any one of them. The laws of thermodynamics tell us what must be known of any substance in order that we may completely know its thermal and dynamical properties. Without thermodynamics we may find the equation of condition of the substance, that is, a relation

$$f(p \cdot v \cdot T) = 0 \tag{1}$$

between the pressure, volume and absolute temperature. This involves dynamical experiments with a manometer at various constant temperatures, and thermometric experiments on the volume at various constant pressures. Thermodynamics puts no restriction on the form of the function f. Now appealing to thermodynamics the first law

$$dQ = dU + pdv = C_x dT + L_x dx \tag{2}$$

in the last member of which C_x and L_x are defined as the specific heat for the parameter x constant, and the latent heat with respect to x, respectively, gives

$$\left(\frac{\partial U}{\partial T}\right)_x = C_x - p\left(\frac{\partial v}{\partial T}\right)_x, \quad \left(\frac{\partial U}{\partial x}\right)_T = L_x - p\left(\frac{\partial v}{\partial x}\right)_T. \tag{3}$$

If the specific heat and latent heat are known completely as functions of any two variables, such as T and p or v, then we can find U the energy, and the properties of the body are known. This involves calorimetric experiments, with two variables. Eliminating U, we have

$$\frac{\partial C_x}{\partial x} - \frac{\partial L_x}{\partial T} = \frac{\partial p}{\partial x}\frac{\partial v}{\partial T} - \frac{\partial p}{\partial T}\frac{\partial v}{\partial x}. \tag{4}$$

The second law of thermodynamics gives

$$dQ = TdS = C_x dT + L_x dx, \tag{5}$$

so that we have

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x, \quad L_x = T\left(\frac{\partial S}{\partial x}\right). \tag{6}$$

Eliminating the S by differentiation,

$$\frac{\partial C_x}{\partial x} - \frac{\partial L_x}{\partial T} = -\frac{L_x}{T}, \tag{7}$$

and combining this equation with the last, we have

$$\frac{L_x}{T} = \frac{\partial p}{\partial T}\frac{\partial v}{\partial x} - \frac{\partial p}{\partial x}\frac{\partial v}{\partial T}, \tag{8}$$

so that L_x is obtained from (8), and need not be investigated experimentally. Knowing thus the partial derivatives of U and S we may obtain both these functions, when all questions about the substance can be answered. In order to fully characterize a substance, then, we require dynamical, thermometric and calorimetric experiments.

Let us now consider the energy. Combining both laws

$$TdS = dU + pdv. \tag{9}$$

Subtracting $d(TS)$ from both sides,

$$d(U - TS) = -pdv - SdT = d\psi, \tag{10}$$

where ψ is one of Gibbs's functions, and Helmholtz's free energy. The condition for a perfect differential gives

$$\frac{\partial S}{\partial v} = \frac{\partial p}{\partial T}. \tag{11}$$

Using this relation in the equation (9), otherwise written,

$$dU = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial v}dv = T\left(\frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial v}dv\right) - pdv, \tag{12}$$

along with (6),

$$T\left(\frac{\partial S}{\partial T}\right)_v = C_v$$

gives

$$dU = C_v dT + \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} dv. \tag{13}$$

If we put

$$p_e = T\left(\frac{\partial p}{\partial T}\right)_v - p, \quad dU = C_v dT + p_e dv, \tag{14}$$

then $p_e dv$ is the work necessary to be done in expanding the gas at constant temperature and stored as energy, and as this is positive

if $p_e > 0$, we may call p_e the cohesion pressure of the gas, due to attraction of the molecules. If $p_e < 0$ the molecules repel each other.

Consider now the porous plug experiment. The conditions of this are that the work of driving the gas into the plug is taken from the energy, the conditions being adiabatic, so that $U + pv$ remains constant through the process of passing through the plug. Now $U + pv$ is Gibbs's function χ. Adding vdp to both sides of (9) we obtain

$$vdp + TdS = d(U + pv) = d\chi. \tag{15}$$

Choosing as variables T, p, the equation for the plug experiment is

$$d\chi = vdp + T\left(\frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial p}dp\right) = 0. \tag{16}$$

Now replace $\partial S/\partial p$ by its equal $-\partial v/\partial T$ obtained by adding $d(pv)$ to (10) to get

$$d\zeta = d(U - TS + pv) = vdp - SdT, \quad \frac{\partial \zeta}{\partial p} = v, \quad \frac{\partial \zeta}{\partial T} = -S \tag{17}$$

and eliminating ζ. Using the definition of C_p in (6),

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{18}$$

we have from (16)

$$\left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\} dp + C_p dT = 0 \tag{19}$$

giving as the measure of the Joule-Kelvin effect

$$K = \frac{dT}{dp} = \left\{ T\left(\frac{\partial v}{\partial T}\right)_p - v \right\} \Big/ C_p. \tag{20}$$

This equation was obtained by Jochmann in 1859.

Let us now consider the three equations:

I. $$pv = RT,$$

II. $$p_e = T\left(\frac{\partial p}{\partial T}\right)_v - p = 0,$$

III. $$C_p K = T\left(\frac{\partial v}{\partial T}\right)_p - v = 0,$$

or the less inclusive than I expressing Boyle's law,

$$I_a. \qquad pv = f(T).$$

If I is true we easily show that II and III are also. Accordingly I is a *sufficient* definition of an ideal gas, but, as has been stated, involves the previous knowledge of the absolute temperature. On the other hand suppose that we have *only* Boyle's law I_a. Then we have

$$(21) \qquad p_e = \frac{1}{v}(Tf'(T) - f(T))$$

$$(22) \qquad C_p K = \frac{1}{p}(Tf'(T) - fT).$$

Consequently *either* of II or III involves the other, and in addition, since we obtain by integration of

$$(23) \qquad Tf'(T) - f(T) = 0, \quad f(T) = RT$$

the product pv *does* measure the absolute temperature. Accordingly Buckingham's definition is both necessary and sufficient, and defines the absolute temperature, but may be replaced by the equivalent specification of Boyle's law and no cohesion, or, what is the same thing, the energy depends wholly on the temperature.

Finally, suppose we disregard the gas laws altogether, and consider only II. Integrating on the supposition $v = const.$, we obtain

$$(24) \qquad \frac{T}{p} = g(v).$$

Such a gas then is suitable for measuring the absolute temperature on a *constant volume* thermometer, but will not, in general, have a zero Joule-Kelvin effect. In like manner, if we suppose III, integrating on the hypothesis of $p = const.$

$$(25) \qquad \frac{T}{v} = h(p),$$

so that such a gas is suited to measure the absolute temperature on a *constant pressure* thermometer, but will, in general, have its energy depend on the volume or pressure as well as on the temperature.

Finally, suppose that II and III hold simultaneously, then by multiplication of (24) and (25)

$$\frac{h(p)}{p} = \frac{g(v)}{v},$$

and as a function of p alone cannot equal a function of v alone, *both* must be constant $1/R$, so that the product pv *does* measure the absolute temperature, and the gas is ideal. Consequently the pair, I_a II, I_a III, or II, III is equivalent to the single equation I and we have three possible definitions of an ideal gas.

Thus it appears that the disappearance of the Joule-Kelvin effect in the plug experiment is *not* a test of absence of cohesion, unless the gas is ideal, and conversely. As an example consider the case instanced by van der Waals as being true for hydrogen,

$$p(v - b) = RT.$$

This evidently comes under (24) so that there is no cohesion and according to this criterion alone the gas would be ideal. Calculating K we have

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = v - b, \quad C_p K = -b,$$

so that the plug effect does not vanish, but is $-b/C_p$, which is of the sign actually found for hydrogen at ordinary temperatures.

No particular originality is claimed for the results here stated, as the far more important problem of determining the absolute temperature when K is known as a function of p, T has been treated in extenso by many authors, but it is believed that the points here made in the last pages have been nowhere explicitly stated.

CLARK UNIVERSITY,
October 23, 1908.

ON THE ABSOLUTE MEASUREMENT OF ELECTRO-MAGNETIC QUANTITIES.

BY V. BJERKNES.

1. The measurement of any physical quantity consists in a comparison with a quantity of the same kind used as unit. Thus every measurement is relative. But using the intrinsic relations existing among quantities of different kinds, we can make the choice of a unit for one quantity dependent upon that for other quantities. Thus the choice of primary units may be reduced to a minimum. As primary units there have been chosen those of length, mass and time, and a quantity is very inadequately said to be measured in absolute measure if the unit of this quantity is fully determined by the choice of units for length, mass and time.

From this it will be evident that the necessary and sufficient condition for the absolute measurement of n independent quantities, in the stated conventional sense of the expression, will demand a knowledge of n independent relations connecting these quantities with others which have already been measured absolutely. If we take any group of physical quantities, introduced to describe a certain class of phenomena, it cannot of course be postulated beforehand that the required number of equations exists. The necessity of introducing new primary units may present itself. But in the following discussion of absolute measurement of that group of quantities which have been introduced to describe the phenomena of the electromagnetic field, we proceed under the explicitly stated hypothesis that in this case no new primary unit is required.

2. To describe electromagnetic phenomena in a homogeneous isotropic dielectric under the simplest conditions, the following six quantities can be used:[1] α and β, respectively the electric and mag-

[1] The notation and terminology are the same as in my Columbia lectures, "Fields of Force," New York, 1906, or the revised German edition of these lectures, "Die Kraftfelder," Braunschweig, 1909. Heaviside's rational units are used consistently.

netic inductivity of the dielectric supporting the field; **A** and **B**, respectively, the electric and magnetic flux (induction); **a** and **b**, respectively, the electric and magnetic field intensity. These quantities satisfy the following equations:

The equations of connection between a flux and the corresponding field intensity

$$(a) \qquad \mathbf{A} = \alpha\mathbf{a}, \quad \mathbf{B} = \beta\mathbf{b}.$$

The equations describing the geometrical structure of the electromagnetic field

$$(b) \qquad \frac{\partial \mathbf{A}}{\partial t} = \operatorname{curl} \mathbf{b}, \quad \frac{\partial \mathbf{B}}{\partial t} = -\operatorname{curl} \mathbf{a},$$
$$\operatorname{div} \mathbf{A} = 0, \qquad \operatorname{div} \mathbf{B} = 0.$$

The equations for the dynamical properties of the electromagnetic field, which for our present purpose can be given the following form:

$$(c) \qquad \varphi_e = \int \tfrac{1}{2}\mathbf{A} \cdot \mathbf{a}\,dt,$$
$$\varphi_m = \int \tfrac{1}{2}\mathbf{B} \cdot \mathbf{b}\,dt,$$

φ_e representing the electric and φ_m the magnetic energy of the field, the volume integration being extended to the whole field.

As is well known the equations (*a*) and (*b*) determine uniquely the geometrical structure of the electromagnetic field at any time, if this structure be given at an initial time, in connection with suitable conditions at the boundary, if the field be limited. Thus from a geometrical point of view the system of equations is perfectly determinate.

Bringing also the equations for the energy into application, we can deduce all known phenomena relating to the mechanical effects or transformations of energy in the field. Thus even in this respect the system of equations seems to be perfectly determinate.

But this determinateness no more exists if the problem be to measure in absolute measure each of the quantities which have been introduced in order to form these equations containing our knowledge of the electromagnetic field.

3. Of the six quantities α, β, **A**, **B**, **a**, **b** two can be eliminated by the equations of connection (*a*). Thus there remain four quantities which should be measured absolutely by use of the relations (*b*) and (*c*).

As is immediately seen, each of the equations (*c*) makes possible one absolute measurement. Considering here only the intrinsic principle of the measurement, not its practical realization, we can imagine the equations to be resolved with respect to the scalar products $\mathbf{A} \cdot \mathbf{a}$ and $\mathbf{B} \cdot \mathbf{b}$, or what is in this case the same thing, the arithmetical products Aa and Bb. Thus measurements of energy combined with space-measurements lead to absolute measurements of the products Aa and Bb. More than this cannot be deduced from the equations (*c*).

Passing to equations (*b*) we see that none of them can be used immediately as the basis of any absolute measurement. They only show how the electromagnetic quantities vary from place to place and from time to time, but give no relations of these quantities to quantities of known nature. One consequence can, however, be drawn from the equations, which gives rise to an absolute measurement. As is well known, it follows from these equations that electromagnetic disturbances are propagated at the speed $1/\sqrt{\alpha\beta}$. Thus the measurement of a velocity of propagation leads to the measurement of the product $\alpha\beta$, the value of this product being equal to the reciprocal of the square of the measured velocity of propagation.

Subject to absolute measurements there are thus only the three products Aa, Bb, $\alpha\beta$; and absolute measurement of each of these quantities separately will not be possible before we have succeeded in measuring absolutely a fourth independent expression formed by the same quantities. This requires the discovery of a fourth independent relation, and until this relation be discovered, we can only define systems of *relative* units for the electrical quantities, obtained by a supplementary choice in addition to the choice of the units of mass, length and time.

4. In order to determine suitable systems of relative units two different choices have been made. Either the electric or the magnetic inductivity of empty space (the free ether) has been given the numerical value 1. The first choice defines the system of electric,

the second the system of magnetic units. Both have by international convention been called systems of absolute units. In what follows we shall avoid this misleading terminology and denote them as the two systems of *relative* units.

However the system of units be defined, the numbers expressing the products Aa, Bb, and $\alpha\beta$ must remain unchanged. Remarking that the products Aa and Bb can also be written $1/\alpha \cdot A^2$ and $1/\beta \cdot B^2$, respectively, αa^2 and βb^2, we find the following rules for passing from the numbers expressing any of our quantities in *one* to the numbers expressing the same quantity in *another* system of units.

1. The numbers expressing electric and magnetic inductivity are changed in inverse proportion to each other.

2. The numbers expressing a flux and the corresponding field intensity are changed in inverse proportion to each other.

3. The number expressing an inductivity is changed in direct proportion to the square of the corresponding flux and in inverse proportion to the square of the corresponding field intensity.

Combining the three rules we finally deduce:

4. The numbers expressing electric flux are changed in the same proportion as those expressing magnetic field intensity, and the numbers expressing electric field intensity are changed in the same proportion as those expressing magnetic flux.

To express the same rules in formulæ, let the index q denote that the quantities are expressed in one and the index r that they are expressed in another system of units, and let it be known that the number expressing an electric flux in the system r is n times greater than the number expressing the same flux in the system q. We then get the following scheme for passing from the numbers expressing our quantities in one to those expressing them in the other of these systems of units

$$(a) \qquad \begin{aligned} A_q &= nA_r, & \alpha_q &= n^2\alpha_r, & B_- &= \frac{1}{n}B_r, \\ a_q &= \frac{1}{n}a_r, & \beta_q &= \frac{1}{n^2}\beta_r, & b_- &= nb_r. \end{aligned}$$

If the index q is referred to the electric and index r to the magnetic system of relative units, we have for free space α_q and β_r both

numerically equal to unity, and α_r and β_q both equal to the reciprocal of the square of the velocity of light. For this case we thus find $n = 3 \times 10^{10}$. If on the other hand q be referred to the magnetic and r to the electric system of units, we have $n = \frac{1}{3} \times 10^{-10}$. The same system of equations will allow us to pass from the numbers expressing our quantities in any of our present relative systems of units to those expressing them in the absolute units defined by no other arbitrary choices than those of length, mass and time.

5. The origin of the indeterminateness occurring in the system of equations 2, (a), (b), (c) most probably comes from an incompleteness of the proper field-equations (b). For these give only one instead of two equations serviceable for the purpose of absolute measurement.

I shall try here a conjecture as to a hypothetical, more complete form of these equations. I have been led to this conjecture by a mechanical representation of the phenomena of the electromagnetic field, which I have recently made the subject of an investigation.[1] But the conjecture does not necessarily presuppose the full identity of the compared mechanical and electromagnetic phenomena. Our only supposition is that the analogy, which has been proved to hold so far as we have hitherto been able to examine it, also holds one step outside this limit.

My conjecture is then that the field equations should have the form

$$(a) \qquad \frac{\partial \mathbf{A}}{\partial t} = \operatorname{curl} \mathbf{b}, \qquad \frac{\partial \mathbf{B}}{\partial t} + \mathbf{a} \bigtriangledown \mathbf{B} = -\operatorname{curl} \mathbf{a},$$

$\mathbf{a} \bigtriangleup \mathbf{B}$ denoting a vector having along the three axes o f x, y, z the components

$$(b) \qquad \begin{aligned} &a_x \frac{\partial B_x}{\partial x} + a_y \frac{\partial B_x}{\partial y} + a_z \frac{\partial B_x}{\partial z}, \\ &a_x \frac{\partial B_y}{\partial x} + a_y \frac{\partial B_y}{\partial y} + a_z \frac{\partial B_y}{\partial z}, \\ &a_x \frac{\partial B_z}{\partial x} + a_y \frac{\partial B_z}{\partial y} + a_z \frac{\partial B_z}{\partial z}. \end{aligned}$$

[1] V. Bjerknes, "Die Kraftfelder," Braunschweig, 1909, Chapter XII. The mechanical representation referred to is an extension of that discussed by Wills, this REVIEW, Vol. 26, p. 220, 1908.

Thus the first of Maxwell's equations, the equation for the electric current, is left unchanged. The second, the equation for the "magnetic current," is completed by the addition of the term $\mathbf{a} \nabla \mathbf{B}$. Thus the extension consists in this: We have two kinds of magnetic current, viz., first the well-known magnetic displacement current, having the current density $\partial \mathbf{B}/\partial t$, and second a magnetic current existing wherever an electric field is superimposed upon a magnetic field. The density of this magnetic current is given by the vector $\mathbf{a} \nabla \mathbf{B}$.

6. Supposing this extended form of Maxwell's equations to be correct, we can at once determine the dimensions of the electromagnetic quantities.

From the second equation of 5, (a) it follows that $\mathbf{a} \nabla \mathbf{B}$ has the same dimensions as curl $\mathbf{a}$. The operations ∇ and curl both corresponding to a division by a length L, we get the dimensional equation $[a][B]=[a]$ or

$$[B]=1.$$

Thus the magnetic flux is of dimensions zero. Remembering now that $Bb = 1/\beta \cdot B^2 = \beta b^2$ has the dimensions of energy divided by a volume or $ML^{-1}T^{-2}$, that $a\beta$ has the dimensions of the reciprocal square of a velocity or $L^{-2}T^2$, and finally that $Aa = 1/a \cdot A^2 = aa^2$ has also the dimensions of energy divided by a volume, we find the following system of dimensions:

$$[A] = ML^{-2}T^{-1}, \quad [a] = ML^{-3}, \quad [B] = M^0L^0T^0,$$
$$[a] = LT^{-1}, \quad [\beta] = M^{-1}LT^2, \quad [b] = ML^{-1}T^{-2}.$$

I leave open the question whether in a case like this the determination of the dimensions of a set of quantities involves a complete specification of their physical nature. But a possible specification is this: $\mathbf{A}$ is the specific momentum (momentum per unit volume or mass transport per square centimeter per second) and $\mathbf{a}$ the velocity of the medium supporting the field; a is the density and β the reciprocal coefficient of elasticity of this medium; $\mathbf{B}$ is the double angle of rotation of an element of this medium, and $\mathbf{b}$ one half of the corresponding specific moment of rotation (moment of rotation per unit volume). Adding that the velocities are directed

along the electric, the axes of rotation along the magnetic lines of force, and that this rotation, which is directed negatively if the positive screw rule be used, is counteracted by a special kind of rotational or gyrostatic elasticity represented by the coefficient of elasticity $1/\beta$, we arrive at the mechanical representation referred to above which has led us to the change in Maxwell's second equation. Leaving open the question as to what degree the introduction of the term $\mathbf{a} \nabla \mathbf{B}$ in Maxwell's second equation involves an accordance of the mechanism of the electromagnetic field with the mechanical representation referred to, we shall in what follows use for convenience a terminology based upon an assumption that this accordance is established.

7. As the mere existence of the term $\mathbf{a} \nabla \mathbf{B}$ in the second Maxwell equation would thus lead to the determination of the dimensions of electromagnetic quantities, the quantitative experimental discovery of a phenomenon depending upon this term would lead to absolute measurement of the quantity B and thus to absolute measurement of all the fundamental quantities of the electromagnetic field.

To consider the simplest case possible, let us produce an homogeneous electric field by use of a condenser formed by two parallel circular discs. Outside this condenser let us place two equally strong cylindrical magnets, facing each other, with poles of the same name. The whole system shall be symmetrical with respect to the common axis of the magnets and the condenser-discs, as well as with respect to a plane normal to this axis, passing through the middle point between the discs. This point which is a neutral point of the magnetic field, may be chosen for origin of coördinates, the axis of symmetry being used as the axis of x, and the axes of y and of z being contained in the plane of symmetry already defined.

We can now use Taylor's theorem in finding the components B_x, B_y, B_z of the magnetic flux in the space surrounding the neutral point. Neglecting terms of the second and higher orders, each component is represented by a linear expression in x, y, z. The origin of coördinates being a neutral point, the constant terms will be equal to zero. The linear expressions can be reduced further by the condition that the coördinate planes are planes of symmetry

of the field. At any two points situated symmetrically with respect to one of these planes the components of the vector tangential to the plane should therefore be directly and the components normal to the plane oppositely equal to each other. Noting this we easily see that the three components are given by

$$(a) \qquad B_x = \left(\frac{\partial B_x}{\partial x}\right)_0 x, \quad B_y = \left(\frac{\partial B_y}{\partial y}\right)_0 y, \quad B_z = \left(\frac{\partial B_z}{\partial z}\right)_0 z.$$

As there is further symmetry round the axis of x, we must have $(\partial B_y/\partial y)_0$ equal to $(\partial B_z/\partial z)_0$. Using this result and the solenoidal condition div $\mathbf{B} = 0$, or

$$\frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} + \frac{\partial B_z}{\partial z} = 0$$

we find that

$$\left(\frac{\partial B_z}{\partial z}\right)_0 = \left(\frac{\partial B_y}{\partial y}\right)_0 = -\tfrac{1}{2}\left(\frac{\partial B_x}{\partial x}\right)_0,$$

showing that the field in the neighborhood of the neutral point is fully specified by the value of the derivatives of the components of B at the neutral point.

Proceeding now to form the expressions 5, (b), we remark that the electric field intensity has no component along the axes of y and z. On the other hand it is seen from the expressions (a), that B_y and B_z have no derivatives with respect to x. Thus only one term of the scheme 5, (b) will be different from zero, namely,

$$(b) \qquad a_x \left(\frac{\partial B_x}{\partial x}\right)_0.$$

Thus in the space between the two condenser-plates we have a magnetic current directed from one plate to the other, and having a current density equal to the product of the field intensity of the homogeneous electric field into the value of the derivatives $(\partial B_x/\partial x)_0$ of the magnetic flux. If this derivative is positive, *i. e.*, if the magnetic poles are both south poles, the magnetic current will have the same direction as the electric field. If both poles be north poles the magnetic current will be directed against the electric field.

Now Maxwell's second equation expresses that a magnetic current surrounds itself with an electric field exactly in the same way as an

electric current surrounds itself with a magnetic field, the only difference being in the rule of signs. The current density (b) in all points of a circle round the axis x and of radius r gives a total magnetic current $\pi r^2 a_x (\partial B_x/\partial x)_0$. This current produces an electric field intensity a' having the line integral $2\pi r a'$ along the circumference of this circle. Identifying these two expressions we get

$$(c) \qquad a' = \tfrac{1}{2} r a \left(\frac{\partial B_x}{\partial x}\right)_0 .$$

The direction of the electric field intensity a' relatively to the magnetic current is given by the negative screw rule.

The field intensity produced by the magnetic current will combine with that of the primary homogeneous electric field. The lines of force of this field will thus be twisted *so as to become screw-lines, forming the angle*

$$(d) \qquad \theta = \frac{a'}{a_x} = \tfrac{1}{2} r \left(\frac{\partial B_x}{\partial x}\right)_0$$

with their primary course. As seen from this expression, the angle of twist is independent of the strength as well as of the direction of the electric field, and dependent only upon the derivative $(\partial B_x/\partial x)_0$ of the magnetic flux. Remembering what has been said above on the signs we see that the lines of force should become left-handed screw-lines if both magnetic poles be south-poles and right-handed if both poles be north-poles. Further it is seen from formula (d) that the angle of twist θ will increase proportionally to the distance r from the axis of rotation, reaching its maximum near the edge of the discs.

Taking into consideration this twist of the electric lines of force, it is easily seen how the magnetic current continues its course: Having arrived at the second condenser-plate, it continues as a surface-current radially outwards; then through the exterior space where the electric field is no more homogeneous, and where the magnetic field can no more be represented by the linear expressions (a), it returns to the first plate, where it goes radially inwards, closing its course.

Equation (d) can now be used for the absolute measurement of magnetic polarization. Let B be the value of this polarization on

the axis of symmetry at the distance l from the neutral point. We then have

$$\left(\frac{\partial B_x}{\partial x}\right)_0 = \frac{B}{l}.$$

Introducing this in equation (d) and solving with respect to B, we get

$$B = 2\theta\frac{l}{r}.$$

This formula is interesting inasmuch as it directly represents the magnetic polarization as a quantity of the nature of an angle. $\frac{1}{2}B$ representing the angle of rotation round a magnetic line of force, we find, putting $l = r$,

$$\tfrac{1}{2}B = \theta.$$

In the field considered therefore the following simple relation exists: The angle of rotation round a magnetic line of force at a point on the axis of symmetry situated at any distance r from the neutral point is equal to the angle of twist of those electric lines of force which are at the distance r from the axis of symmetry.

Measuring the angle of twist θ of the electrical lines of force, we thus get an absolute measurement of $\frac{1}{2}B$ and thus of B. Supposing that we measure this same magnetic flux in relative magnetic measure we get a comparison of this measure with the absolute measure. Let B_m be the number which expresses the flux in magnetic measure, and let this number be n times greater than the number B expressing it in absolute measure. We then have

$$B = \frac{1}{n}B_m.$$

Afterwards by equation 4, (a) we find the corresponding relations for the other quantities.

8. Using the means which I had at hand, I have performed the experiment of which I have thus indicated the principle. The result being negative inasmuch as no angle of twist θ of the electric lines of force could be detected, it will be of no interest to enter into a detailed description. I therefore only give these summary indications.

Two cylindrical electromagnets were used, the iron cores of which had a length of about 40 and a diameter of 7.5 cm. On these cores was coiled a 3 cm. thick and 34 cm. long layer of copper wire. The current was furnished by a generator delivering 30, or, when forced, 50 amperes at the pressure of 4 volts. The condenser-discs had the same diameter as the cores of the magnets and were placed 2 cm. apart. At the upper edge of the discs, at 3.5 cm. distance from the axis, was suspended a light aluminium needle carrying a mirror. At the distance of 2 meters scale and telescope were placed.

The condenser plates were charged to opposite potentials varying from 1,000 to 2,000 volts. In the field thus produced the needle was held strongly in a position of equilibrium, being directed along the lines of force. The magnetic field was then put on, alternately, so that two south-poles or two north-poles were facing each other. The change from the one case to the other should cause a change of direction of the electrical lines of force of 2θ, and the needle pointing always in the direction of the lines of force should show the same deflection.

All causes of disturbance being carefully removed, or their effect being eliminated by special measurements (direct magnetic effect on the needle, small disturbances of the electric field), it was established that the hypothetical double-deflection could not reach two tenths of a millimeter. Thus the angle θ did not exceed $\frac{1}{40000}$ radian. Hence the rotation round a magnetic line of force at a point situated on the axis of symmetry at the distance of 3.5 cm. from the neutral point could not exceed $\frac{1}{40000}$. The value of B at this point being equal to twice this angle, the result of the measurement gives for the magnetic flux at the place indicated

$$B < \tfrac{1}{20000} \text{ cm.}^0 \text{ gr.}^0 \text{ sec.}^0$$

The ends of the magnets were at the distance of 1.75 cm. from the neutral point. Using the Lenard spiral the flux at the surface of the magnets was found equal to about 180 irrational magnetic units of flux. Passing to Heaviside's rational units, which we have used consistently in the preceding, we have to divide this number by $\sqrt{4\pi}$. Thus the flux at the surface of the magnets was about

50 rational magnetic units. If the field had extended to double the distance of 3.5 cm. from the neutral point, we should have had the field-intensity 100. Thus

$$B_m = 100 \text{ rational magnetic units.}$$

The number expressing a magnetic flux in magnetic measure is thus at least two million times greater than that expressing the same flux in absolute measure. We then have to introduce in equations 4, (*a*) $n > 2 \times 10^6$, and get as a result the scheme

$$A > 2 \times 10^6 A_m, \quad a > 4 \times 10^{12} a_m, \quad B < \tfrac{1}{2} \times 10^{-6} B_m,$$
$$a < \tfrac{1}{2} \times 10^{-6} a_m, \quad \beta < \tfrac{1}{4} \times 10^{-12} \beta_m, \quad b > 2 \times 10^6 b_m.$$

Using the scheme 4, (*a*) once more, to pass from the numbers expressing our quantities in magnetic to those expressing them in electric units, we get $n = \frac{3}{8} \times 10^{-4}$ and thus

$$A > \tfrac{3}{8} \times 10^{-4} A_e, \quad a > \tfrac{4}{9} \times 10^{-8} a_e, \quad B < \tfrac{3}{2} \times 10^4 B_e,$$
$$a < \tfrac{3}{2} \times 10^4 a_e, \quad \beta < \tfrac{9}{4} \times 10^8 \beta_e, \quad b > \tfrac{3}{8} \times 10^{-4} b_e.$$

To consider more closely the content of some of these equations, we remark that in the free ether $a_e = 1$. Thus the absolute electric inductivity or the density of the ether is greater than $\frac{4}{9} \times 10^{-8}$ grams per cubic centimeter. Further in the free ether we have $\beta_m = 1$. Thus the absolute magnetic inductivity or the reciprocal coefficient of elasticity of the free ether is smaller than $\frac{1}{4} \times 10^{-12}$ gr.$^{-1}$ cm. sec.^{2} Or the coefficient of elasticity of the ether is greater than 4×10^{12} gr. cm.$^{-1}$ sec.$^{-2}$, *i. e.*, dynes per square centimeter. Putting $a_e = 1$, we get $a < \frac{3}{2} \times 10^4$, *i. e.*, the velocity corresponding to the rational electric unit of electric field intensity is smaller than $\frac{3}{2} \times 10^4$ centimeters per second. $A_e = 1$ gives the corresponding value of A greater than $\frac{3}{8} \times 10^{-4}$, *i. e.*, the specific momentum corresponding to the rational electric unit of electric flux is a transport of mass greater than $\frac{3}{2} \times 10^{-4}$ grams per square cm. per second. Putting $B_m = 1$ we get the corresponding value of B smaller than $\frac{1}{2} \times 10^{-6}$, *i. e.*, the double angle of rotation corresponding to the rational magnetic unit of magnetic flux is smaller than $\frac{1}{2} \times 10^{-6}$ radian. Setting finally $b_m = 1$ we get the corresponding value of b greater than 2×10^6,

i. e., the half torque per unit volume, which represents the rational magnetic unit of field intensity, is greater than 2×10^6 dynes-centimeter per cubic centimeter.

9. Repeating the experiment described there would be no difficulty in increasing the accuracy far beyond the limit reached in this first attempt. Coiling more wire upon the magnets, and using the strongest current which the coil can support for a short interval of time, it would probably be possible to increase ten times or more the value of the derivative $(\partial B_x/\partial x)_0$ and thus of the angle θ. On the other hand, if the experiment be performed at a place perfectly free from shaking (I only succeeded in getting satisfactory readings thanks to a strong snow-fall, after which the shaking produced by the traffic on the streets was very much reduced), it ought to be possible, using a powerful telescope, to increase ten times the accuracy of the readings. Finally, we can get, theoretically, infinite increase of the effect by increasing the diameter of the iron-cores and the condenser-discs. Far more delicate methods for detecting the electric field intensity a' than that of measuring the angle of twist θ can also be used. Finally, new arrangements can be devised, which may have advantages over the arrangement used in this experiment, which was chosen especially on account of its theoretical simplicity. To mention only one example, an experiment analogous to that of Hall could be performed. The magnets should then have opposite poles facing each other, and the lines of magnetic force should cut those of electric force at right angles. This arrangement would be much more advantageous for the production of a powerful magnetic field.

The higher the accuracy brought into application not leading to the discovery of the effect, the greater must be the value of the density of the ether. With this increasing density follows a decreasing value of the velocity corresponding to the present unit of electric field-intensity and an increasing value of the specific momentum corresponding to the present unit of electric flux. Further, there would follow with increasing density increasing values of the coefficient of elasticity $1/\beta$ of the ether, increasing values of the half torque corresponding to the present unit of magnetic field intensity and decreasing values of the double angle of rotation corresponding to the present relative unit of magnetic flux.

Sir Oliver Lodge has recently produced interesting arguments in favor of an ether-density of the order of magnitude of 10^{12} grams per cubic centimeter, thus 10^{20} times greater than the limit arrived at above. If this estimate be correct, the angle of twist of the electric lines of force really occurring in our experiment would be 10^{10} times smaller than the limit found by us. To discover this angle under the supposition of ten times increased values of $(\partial B_z/\partial x)_0$ and ten times increased accuracy of the reading, we should have to use iron-cores and condenser-discs having a diameter equal to the radius of the earth. Under these conditions the prospect of discovering the effect using the stationary or static fields produced by ordinary means would be very small. The only way out would then probably be the application of the enormously intense magnetic field existing in the immediate neighborhood of a moving negative corpuscle. The first thing to investigate would then be the motion of the corpuscle itself, the new term introduced in Maxwell's equations being taken into account.

10. It should be emphasized in this connection that the view of the mechanical nature of the electromagnetic field which has led Sir Oliver Lodge to his conclusions is different from ours, inasmuch as he explains the magnetic field by motions along the magnetic lines of force and the electric field by rotations round the electric lines of force. Nevertheless his arguments in favor of the ether density 10^{12} will be equally legitimate in both cases. But the method of bringing about an experimental test of the question would be somewhat different. From Lodge's theory, which is essentially the same as that of Larmor and Sommerfeld, we find that Maxwell's equations should have the form

$$(a) \qquad \frac{\partial \mathbf{A}}{\partial t} + \mathbf{b}\nabla\mathbf{A} = \text{curl } \mathbf{b}, \quad \frac{\partial \mathbf{B}}{\partial t} = -\text{curl } \mathbf{a}.$$

The term $\mathbf{b}\nabla\mathbf{A}$ represents a new form of electric, not of magnetic current. While, according to the previous equations 5, (a), a static or stationary electric field will be distorted when a magnetic field is superimposed upon it, we derive from these new equations (a) that a static or stationary magnetic field should be distorted if an electric field be superimposed upon it.

In attempting to discover this distortion, we can use the same experimental arrangement as above, only letting the magnetic field be a homogeneous one, produced by opposite poles N, S of the magnets, while an electric field of the same character as the previously used magnetic one could be produced by charging both discs to the same potential. A slightly magnetic needle might be used, held strongly in equilibrium along the magnetic lines of force. These lines should be twisted into screw lines when the electric field is produced, the screw lines having positive twist if both discs be charged positively. Changing from a positive to a negative charge, the needle should get a deflection equal to the double angle of twist. I have performed this experiment qualitatively, without being able to discover any deflection. I mention it in order to emphasize that the two different views as to the correspondence between electromagnetic and mechanical quantities lead to parallel methods for solving the problem of absolute measurements. One of the experiments having given a positive result, we should arrive at a decision regarding the two different views.

THE MOLECULAR AND THE FRICTIONAL FLOW OF GASES IN TUBES.

By Willard J. Fisher.

IN 1866 O. E. Meyer[1] integrated approximately the equations for the flow of a viscous gas through a circular capillary tube, obtaining the following equation

$$F = \frac{\pi R^4}{16\eta L p}\left(1 + \frac{4\zeta}{R}\right)(p_1^2 - p_2^2),$$

in which F is the volume of gas passing per second, measured at pressure p, R is the radius, L the length of the tube, ζ the slip coefficient, p_1 the entrance, p_2 the exit pressure, η the coefficient of viscosity. He also showed[2] that ζ is equal to the mean free path of the molecule. This varies inversely as the pressure, which, of course, is not the same throughout the tube; an average value of ζ may be used, computed from the kinetic theory equations for pressure and viscosity, and the two measured end pressures. A not very satisfactory derivation of the value of ζ was given by E. Warburg,[3] a better one by A. Bestelmeyer,[4] who showed that the proper pressure to use is the arithmetical mean of the entrance and exit pressures. Using this value of the mean pressure and the kinetic theory relations, O. E. Meyer's equation reduces to

$$F = \left[\frac{\pi R^4}{16\eta L} + \frac{\pi\sqrt{3}}{2}\frac{R^3}{L(p_1 + p_2)\sqrt{\rho_1}}\right](p_1^2 - p_2^2),$$

in which ρ_1 denotes the density of the gas at a pressure of 1 dyne per square centimeter and the temperature of the tube. The numerical factor $\pi\sqrt{3}/2$ has the value 2.72.

M. Knudsen,[5] of Copenhagen, has recently published a theoretical and experimental study of the flow of gases through capillary tubes, with pressures ranging from ordinary to one or two thousandths of

[1] O. E. Meyer, Pogg. Ann., 127, p. 269, 1866.

[2] O. E. Meyer, Kinetic Theory of Gases, English by R. E. Baynes, p. 211.

[3] E. Warburg, Pogg. Annalen, 159, p. 399, 1876.

[4] A. Bestelmeyer, Ann. d. Physik, 13, p. 980, 1904; see also Phys. Rev., 28, p. 73, 1909.

[5] M. Knudsen, Ann. d. Physik, 28, p. 75, 1909.

a millimeter, or, in other words, under conditions such that the mean free path is varied from values very small in relation to the radius of the tube to others very large in relation to the radius. The flow of the gases was then in part the well-known viscous flow, at the other extreme a flow in which the *slip* on the walls is the whole motion, and between an intermediate, mixed state. The two distinct states he calls *molecular flow* and *frictional flow*, which seem to be well-selected and descriptive names. To represent his results he uses the following formula :

$$Q_t = \left[ap + b\frac{1 + c_1 p}{1 + c_2 p} \right](p_1 - p_2),$$

in which

$$Q_t = pF,$$

$$a = \frac{\pi R^4}{8\eta L},$$

the coefficient of frictional flow,

$$b = \frac{4\sqrt{2\pi}}{3}\frac{R^3}{L\sqrt{\rho_1}},$$

the coefficient of molecular flow, derived from his theory; c_1 and c_2 are constants for a given tube-radius and temperature. They have the ratio 2/2.47, as found by Least Squares. $p = (p_1 + p_2)/2$, L and R are the length and radius of the tube.

The equation may readily be compared with that of O. E. Meyer if written

$$Q_t = \left[\frac{\pi R^4}{16\eta L} + \frac{4\sqrt{2\pi}}{3}\frac{R^3}{L(p_1 + p_2)\sqrt{\rho_1}}\frac{1 + c_1 p}{1 + c_2 p} \right](p_1^2 - p_2^2).$$

The numerical factor $4\sqrt{2\pi}/3$ has the value 3.34. The fraction

$$\frac{1 + c_1 p}{1 + c_2 p}$$

is designed so as to equal 1 for large values of p, c_1/c_2 for small and vanishing values; it therefore varies from 1 to about 0.8.

Knudsen's curve for CO_2 is plotted with ordinates $T = Q_t/(p_1 - p_2)$, abscissas $p = (p_1 + p_2)/2$, and shows a decided minimum in the region where p becomes comparable with the saturation pressure of mercury vapor. While others have not studied the flow at as low pressures as Knudsen, and so their results are not strictly comparable, it is interesting to note that previous results on mixtures of light

and dense gases as those of J. Puluj[1] and P. Breitenbach[2] on H and CO_2, and of P. Tänzler[3] on He and Ar, show that the viscosity coefficient has a maximum value not for either pure gas but for a mixture of the two, the position of the maximum depending on the temperature. Hence for such mixtures Knudsen's T would show a minimum, if we imagine an experiment carried on in which $(p_1 + p_2)/2$ would be continually diminished, while at the same time the per cent. of heavy gas were increased. This imaginary case and Knudsen's experiments are not exactly parallel, but show the necessity of caution and a more careful elimination of the mixture effect, even at low pressures.

It will be observed that for large pressures the two equations of O. E. Meyer and Knudsen are identical, for $3.34 \times 2.00/2.47 = 2.70$, and in all other respects they are exactly alike. For lower pressures the factor

$$\frac{1 + c_1 p}{1 + c_2 p}$$

comes into play; but as shown above, this is of relatively small importance. It is not at all unlikely that the need of this factor is due to a defect in the experimental method.

The experiments were carried on at practically constant temperature; gas passed directly from contact with a free mercury surface through the tube, carrying with it saturated mercury vapor. At ordinary pressures this usually forms a negligible factor, but when the pressures approach or even fall below the pressure of saturated mercury vapor it is certain that a very important part of the substance passing through the tube is not the gas in question at all; Knudsen's observations at low pressure relate then, not to the molecular flow of gases but to the flow of varying mixtures of gases and mercury vapor. Were the vapor disturbance eliminated it is not at all improbable that the results would be very well expressed by the long-known formula of O. E. Meyer.

It is to be hoped that improvements in the method of observation may be made, as investigations in this region are of much promise.

GÖTTINGEN, June, 1909.

[1] J. Puluj, Carls Rep., 15, pp. 518, 633, 1879.
[2] P. Breitenbach, Wied. Ann., 67, p. 820, 1899.
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